*Organometallics* 1992, *11*, 3534–3542

# Metalloradical Reactions of Rhodium(II) Porphyrins with Acrylates: Reduction, Coupling, and Photopromoted Polymerization

Bradford B. Wayland* and George Poszmik

*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323*

Michael Fryd

*Marshall Laboratories, E.I. du Pont de Nemours and Company, Philadelphia, Pennsylvania 19146*

*Received April 9, 1992*

(Octaethylporphyrinato)rhodium(II) dimer, $[(\text{OEP})\text{Rh}]_2$, adds with acrylates and reduces the alkene unit in forming two-carbon-alkyl-bridged complexes $(\text{OEP})\text{RhCH}_2\text{CH}(\text{CO}_2\text{X})\text{Rh}(\text{OEP})$ ($\text{X} = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}_3$). Stereoisomers resulting from inhibition of rotation around the $\text{C–CO}_2\text{X}$ bond wedged between two porphyrin rings are observed and discussed. Steric demands of tetramesitylporphyrin (TMP) preclude dimerization of $(\text{TMP})\text{Rh}^\bullet$, inhibit formation of two-carbon-alkyl-bridged complexes, and promote alkene coupling in reactions of $(\text{TMP})\text{Rh}^\bullet$ with acrylates. The resulting four-carbon-alkyl-bridged complexes $(\text{TMP})\text{RhCH}_2\text{CH}(\text{CO}_2\text{X})\text{CH}(\text{CO}_2\text{X})\text{CH}_2\text{Rh}(\text{TMP})$ form exclusively with an alkyl fragment produced from head to head alkene dimerization. The presence of two chiral centers results in diastereomers observed by $^1\text{H}$ NMR. Rhodium(II) porphyrins react with methyl methacrylate to form alkenyl derivatives $(\text{por})\text{RhCH}_2\text{C}(\text{CO}_2\text{CH}_3){=}\text{CH}_2$ and an equal quantity of either a hydride or alkyl complex by a process related to alkyl radical disproportionation. Rhodium(II) porphyrin metalloradicals, $(\text{por})\text{Rh}^\bullet$, are ineffective at initiating thermal polymerization of acrylates, but the (TMP)Rh system catalyzes a photopromoted polymerization of acrylates that has living character. A thermochemical model is used in unifying and discussing the observed reactions of acrylates with rhodium(II) porphyrins.

## Introduction

Rhodium(II) porphyrins and related macrocycle complexes are sources of low-spin $d^7$ ($s = {}^1/_2$) species that characteristically manifest one-electron radical-like reactivity patterns.[1-3] Formation of relatively strong Rh–C bonds, which approach 60 kcal $\text{mol}^{-1}$ in organometallic derivatives of rhodium porphyrins,[4-6] provides this class of complexes with a currently unparalleled scope of metalloradical reactions. One example of this behavior is illustrated by reactions with alkenes that form two-carbon-$\text{sp}^3$-hybridized-alkyl-bridged ($\mu,\eta^1\eta^1$) complexes (eq 1).[7-9] This general type of alkene reaction has also been

$$2(\text{por})\text{Rh}^{\text{II}\bullet} + \text{CH}_2{=}\text{CH(X)} \rightleftharpoons (\text{por})\text{RhCH}_2\text{CH(X)Rh(por)} \tag{1}$$

observed for iridium(II) porphyrins,[10] and in the reaction of the highly activated tetrafluoroethylene with $\text{Co}_2(\text{CO})_8$.[11] Alkene reactions with single metal centers that produce metallocyclopropanes[12] and multiple M–M bonded complexes that form dimetallacyclobutanes[13] and reactions that form $\mu,\eta^2\eta^2$ structures[14] where each metal site is equidistant from the two bridging carbons are also similar to reaction 1.

Kinetic studies for the reaction of (octaethylporphyrinato)rhodium(II) dimer, $[(\text{OEP})\text{Rh}]_2$ (1), with styrene to form $(\text{OEP})\text{RhCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{Rh}(\text{OEP})$ have been interpreted in terms of a radical-like chain process involving an organometallic intermediate that reacts in a manner similar to that expected for a carbon-centered radical, $(\text{OEP})\text{Rh-CH}_2\dot{\text{C}}\text{H}(\text{C}_6\text{H}_5)$ (eqs 2–4).[3] Products of

$$[(\text{OEP})\text{Rh}]_2 \rightleftharpoons 2(\text{OEP})\text{Rh}^\bullet \tag{2}$$

$$(\text{OEP})\text{Rh}^\bullet + \text{CH}_2{=}\text{CH}(\text{C}_6\text{H}_5) \rightleftharpoons [(\text{OEP})\text{RhCH}_2\dot{\text{C}}\text{H}(\text{C}_6\text{H}_5)] \tag{3}$$

$$[(\text{OEP})\text{RhCH}_2\dot{\text{C}}\text{H}(\text{C}_6\text{H}_5)] + [(\text{OEP})\text{Rh}]_2 \rightleftharpoons (\text{OEP})\text{RhCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{Rh}(\text{OEP}) + (\text{OEP})\text{Rh}^\bullet \tag{4}$$

the reaction of propene with $[(\text{OEP})\text{Rh}]_2$ also have a formal resemblance to radical coupling and disproportionation processes expected for a carbon-centered organometallic radical intermediate, $(\text{OEP})\text{RhCH}_2\dot{\text{C}}\text{HCH}_3$.[7]

---

[1] Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* 1981, 475.

[2] (a) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* 1989, *111*, 5010. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* 1991, *113*, 5305. (c) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* 1990, *112*, 1259.

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

[4] (a) Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* 1986, *108*, 3659. (b) Wayland, B. B.; Farnos, M. D.; Coffin, V. L. *Inorg. Chem.* 1988, *27*, 2745. (c) Coffin, V. L.; Brennen, W.; Wayland, B. B. *J. Am. Chem. Soc.* 1988, *110*, 6063.

[5] Wayland, B. B. *Polyhedron* 1988, *7*, 1545.

[6] Wayland, B. B.; Coffin, V. L.; Sherry, A. E.; Brennen, W. R. ACS Symposium Series 428; Marks, T., Ed.; American Chemical Society: Washington, DC, 1990; Chapter 10, pp 148–158.

[7] Wayland, B. B.; Ba, S. *Organometallics* 1989, *8*, 1438.

[8] Ogoshi, H.; Setsume, J.; Yoshida, Z. *J. Am. Chem. Soc.* 1977, *99*, 3869.

[9] Van Voorhees, S. L.; Wayland, B. B. *Organometallics* 1987, *6*, 204.

[10] Del Rossi, K. J.; Wayland, B. B. *J. Chem. Soc., Chem. Commun.* 1986, 1653.

[11] (a) Hoehn, H. H.; Pratt, L.; Watterson, K. F.; Wilkinson, G. *J. Chem. Soc.* 1961, 2738. (b) Booth, B. L.; Haszeldine, R. N.; Mitchell, P. R.; Cox, J. J. *J. Chem. Soc.* 1969, 691.

[12] (a) Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta.* 1963, *46*, 1588. (b) Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 3, Chapter 19.

[13] (a) Burke, M. R.; Takats, J.; Grevels, F. W.; Reuben, J. G. A. *J. Am. Chem. Soc.* 1983, *105*, 4092. (b) Anderson, O. P.; Bender, B. R.; Norton, J. R.; Larson, A. C.; Vergamini, P. J. *Organometallics* 1991, *10*, 3145.

[14] (a) Burns, C. J.; Anderson, R. A. *J. Am. Chem. Soc.* 1987, *109*, 915. (b) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* 1990, *112*, 219.

0276-7333/92/2311-3534$03.00/0

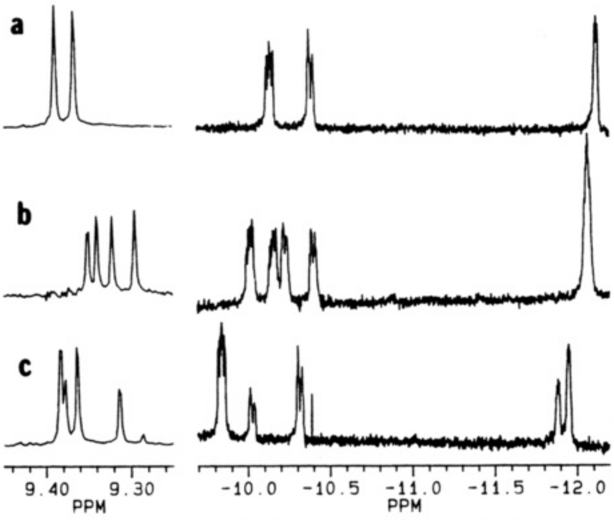


**Figure 1.** $^1$H NMR (500 MHz) spectra for the porphyrin methyne and high-field bridging alkyl resonances for derivatives of **3** ((OEP)RhCH$_2$CH(CO$_2$X)Rh(OEP)) produced by reaction 5 (300 K in C$_6$D$_6$): (a) X = H; (b) X = CH$_3$; (c) X = CH$_2$CH$_3$.

These previous observations suggested that reactions of alkenes with rhodium(II) porphyrins might provide controlled sources of metalloorganic radicals MCH$_2\dot{C}$H(X) which could be intercepted by alkenes to form alkene dimers, oligomers, and polymers. This paper defines the scope of acrylate thermal reactions with rhodium(II) porphyrins, and further reports on a photopromoted polymerization of acrylates that is catalyzed by (tetramesitylporphyrinato)rhodium(II), (TMP)Rh$^\bullet$ (**2**).

## Results and Discussion

**Reactions of [(OEP)Rh]$_2$ with Acrylates CH$_2$=CH(CO$_2$X) (X = H, CH$_3$, CH$_2$CH$_3$).** [(OEP)Rh]$_2$ (**1**) reacts reversibly with acrylates to form two-carbon-alkyl-bridged complexes (OEP)RhCH$_2$CH(CO$_2$X)Rh(OEP) (**3**) (eq 5) as

$$[(\mathrm{OEP})\mathrm{Rh}]_2 + \mathrm{CH_2{=}CH(CO_2X)} \rightleftharpoons \underset{\mathbf{3}}{(\mathrm{OEP})\mathrm{RhCH_2CH(CO_2X)Rh(OEP)}} \quad (5)$$

the only $^1$H NMR observable product. The acrylic acid derivative of **3**, (OEP)RhCH$_2$CH(CO$_2$H)Rh(OEP), occurs as a single $^1$H NMR observable species, but the methyl and ethyl acrylate derivatives of **3** each occur as two isomers in approximately 1/1 and 2/1 ratios, respectively (Figure 1). The isomerization is ascribed to the two orientations of the carboxylate OR group which arises from inhibited rotation around the C–CO$_2$R bond. The carboxylate group is trapped between two porphyrins such that the orientations of the carboxylate OR group toward or away from the more distant porphyrin do not interchange rapidly on the NMR time scale (Figure 2). Rotation around the C–CO$_2$H bond in the acrylic acid derivative of **3** should also be inhibited, and thus observation of a single isomer is ascribed to either having a symmetrical hydrogen position or rapid hydrogen exchange between the carboxylate oxygens.

In order to gain further evidence for this type of stereoisomerism, the two-carbon-alkyl-bridged complexes derived from reaction of styrene and 3-methylstyrene with [(OEP)Rh]$_2$ were examined. The styrene complex (OEP)RhCH$_2$CH(C$_6$H$_5$)Rh(OEP) occurs as a single isomer, but observation of five inequivalent phenyl hydrogens in the $^1$H NMR is indicative of inhibited rotation around the C–C$_6$H$_5$ bond. Substituting a methyl group on the 3-position of phenyl produces inequivalent sides of the phenyl group, and two isomers are observed for (OEP)RhCH$_2$CH(C$_6$H$_4$(CH$_3$))Rh(OEP) in accord with the rotamer model proposed for derivatives of **3**.

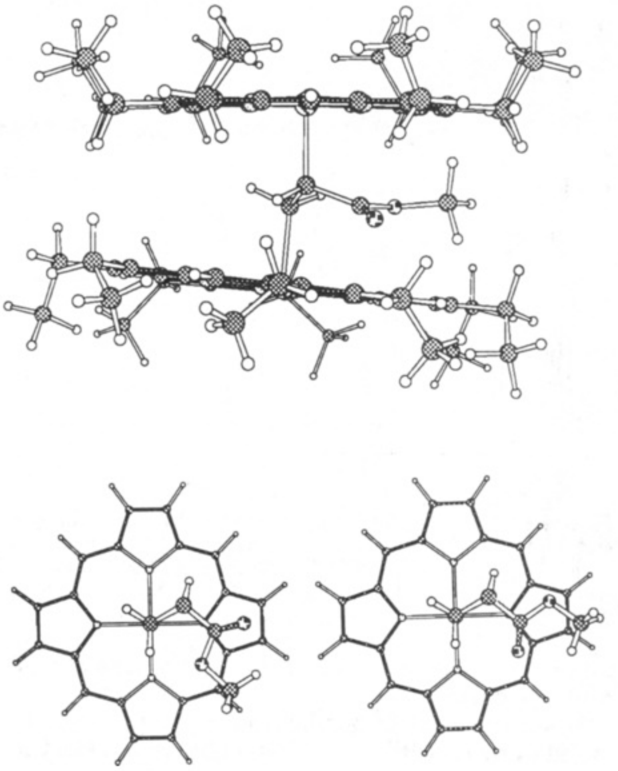


**Figure 2.** Structure simulation of (OEP)RhCH$_2$CH(CO$_2$CH$_3$)-Rh(OEP) and illustration of the two isomers resulting from inhibition of rotation around the C–CO$_2$CH$_3$ bond.

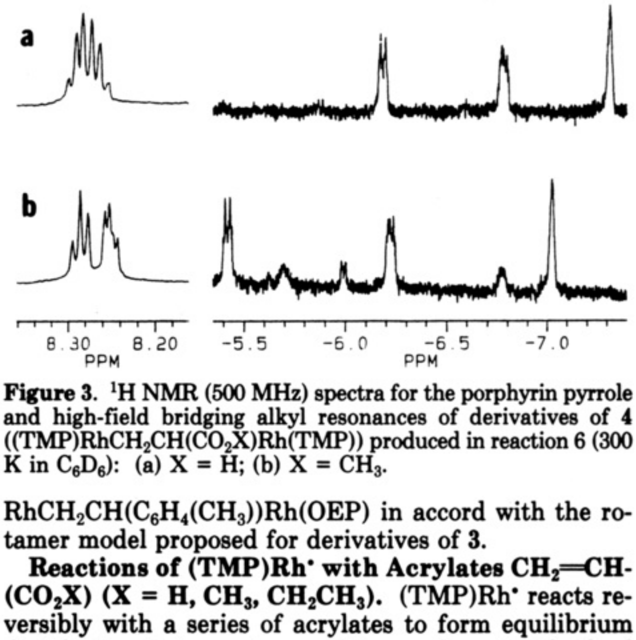


**Figure 3.** $^1$H NMR (500 MHz) spectra for the porphyrin pyrrole and high-field bridging alkyl resonances of derivatives of **4** ((TMP)RhCH$_2$CH(CO$_2$X)Rh(TMP)) produced in reaction 6 (300 K in C$_6$D$_6$): (a) X = H; (b) X = CH$_3$.

**Reactions of (TMP)Rh$^\bullet$ with Acrylates CH$_2$=CH(CO$_2$X) (X = H, CH$_3$, CH$_2$CH$_3$).** (TMP)Rh$^\bullet$ reacts reversibly with a series of acrylates to form equilibrium distributions between two- and four-carbon-alkyl-bridged complexes (eqs 6 and 7). The two-carbon-alkyl-bridged

$$2(\mathrm{TMP})\mathrm{Rh}^\bullet + \mathrm{CH_2{=}CH(CO_2X)} \rightleftharpoons \underset{\mathbf{4}}{(\mathrm{TMP})\mathrm{RhCH_2CH(CO_2X)Rh(TMP)}} \quad (6)$$

$$2(\mathrm{TMP})\mathrm{Rh}^\bullet + 2\mathrm{CH_2{=}CH(CO_2X)} \rightleftharpoons \underset{\mathbf{5}}{(\mathrm{TMP})\mathrm{RhCH_2CH(CO_2X)CH(CO_2X)CH_2Rh(TMP)}} \quad (7)$$

complexes (TMP)RhCH$_2$CH(CO$_2$X)Rh(TMP) (**4**) are closely related to the (OEP)Rh derivatives of **3** except that only one rotational isomer is observed by $^1$H NMR (Figure 3). The increased steric requirements of TMP compared with OEP apparently produce an additional perturbation that favors one of the two possible carboxylate OR orien-

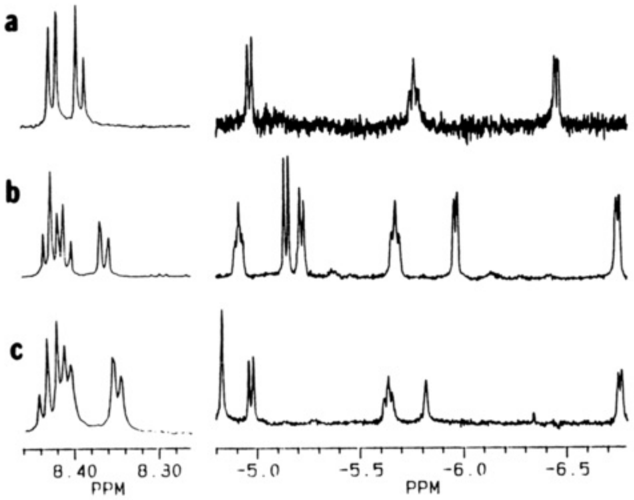


**Figure 4.** $^1H$ NMR (500 MHz) spectra for the porphyrin pyrrole and high-field bridging alkyl resonances of derivatives of **5** ((TMP)RhCH$_2$CH(CO$_2$X)CH(CO$_2$X)CH$_2$Rh(TMP)) produced in reaction 7 (300 K in $C_6D_6$): (a) X = H; (b) X = CH$_3$; (c) X = CH$_2$CH$_3$.

tations such that only one of the orientations is significantly populated.

When an excess of acrylic acid or methyl acrylate is mixed with (TMP)Rh$^\bullet$ ($\sim 10^{-3}$ M) in benzene, a kinetically determined distribution of the two- and four-carbon-bridged complexes **4** and **5** is rapidly formed. A slower subsequent reaction converts **4** into an equilibrium distribution of **4** and **5** (eq 8). This behavior is consistent

$$\mathbf{4} + CH_2{=}CH(CO_2X) \rightleftharpoons \mathbf{5} \qquad (8)$$

with the two- and four-carbon-bridged complexes **4** and **5** forming through a common intermediate which we believe is a metalloradical–alkene complex, [(TMP)Rh(CH$_2$=CH(CO$_2$X))]$^\bullet$ (**6**). The initial distribution of compounds **4** and **5** can be viewed as forming by rapid reactions of **6** with either a second (TMP)Rh$^\bullet$ or dimerization (eqs 9–11). The slower reaction that ultimately produces

$$(TMP)Rh^\bullet + CH_2{=}CH(CO_2X) \rightleftharpoons \underset{\mathbf{6}}{[(TMP)Rh(CH_2{=}CH(CO_2X))]^\bullet} \qquad (9)$$

$$\mathbf{6} + (TMP)Rh^\bullet \rightleftharpoons \underset{\mathbf{4}}{(TMP)RhCH_2CH(CO_2X)Rh(TMP)} \qquad (10)$$

$$\mathbf{6} + \mathbf{6} \rightleftharpoons \underset{\mathbf{5}}{(TMP)RhCH_2CH(CO_2X)CH(CO_2X)CH_2Rh(TMP)} \qquad (11)$$

an equilibrium between **4** and **5** probably proceeds through the formation of **6** by dissociation of a (TMP)Rh$^\bullet$ unit from **4**. Differences in the steric demands of the –CO$_2$H, –CO$_2$CH$_3$, and –CO$_2$CH$_2$CH$_3$ groups are clearly illustrated by the equilibrium distributions of the alkyl-bridged complexes. In the acrylic acid containing system, the two-carbon-bridged complex is the major product at small excesses of acrylic acid (alkene/Rh < 10), and the four-carbon-bridged complex predominates only at large excesses (alkene/Rh > 200). In the case of methyl acrylate the four-carbon-bridged complex is the major thermodynamic product even at close to a stoichiometric ratio of (TMP)Rh$^\bullet$ and methyl acrylate (Figure 4). Following this trend, the reaction of ethyl acrylate with (TMP)Rh$^\bullet$ yields the four-carbon-bridged complex as the only NMR observable product even at less than 1/1 stoichiometry (alkene/Rh < 1).

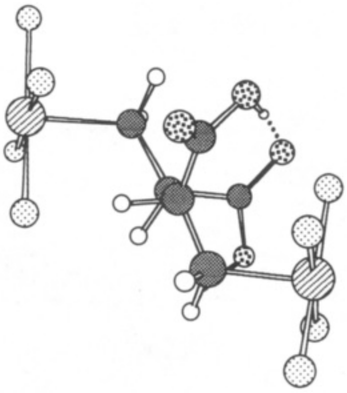


**Figure 5.** Structure simulation of the optically active isomer of (TMP)RhCH$_2$CH(CO$_2$H)CH(CO$_2$H)CH$_2$Rh(TMP) showing the potential hydrogen bonding between the two –CO$_2$H groups (porphyrin ligands omitted for clarity).

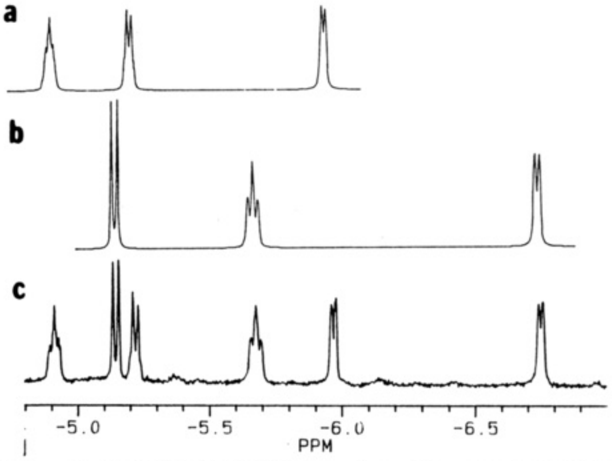


**Figure 6.** $^1H$ NMR (500 MHz) spectra of the alkyl bridge hydrogen resonances for the methyl acrylate derivatives of **5**: (a) simulation for the meso isomer; (b) simulation for the optically active isomer; (c) observed spectrum.

The presence of two centers of chirality in compounds of type **5** produce meso and optically active diastereomers which are observed for the methyl and ethyl acrylate derivatives of **5**. The preferred conformations have (TMP)RhCH$_2$– groups in anti positions such that the optically active diastereomer has –CO$_2$R groups in gauche positions and the meso form has anti –CO$_2$R groups. The sequence of reactions that result in producing derivatives of **5** are readily reversible, and thus equilibrium distributions of isomers are ultimately attained. The acrylic acid derivative of **5** has only one $^1H$ NMR observable diastereomer which is tentatively assigned to the optically active form with gauche –CO$_2$H groups. Placing the –CO$_2$H groups in gauche positions allows hydrogen bonding between the carboxylic acid groups which probably accounts for observing only one diastereomer (Figure 5).

Assignments for the meso and optically active diastereomers of the methyl and ethyl acrylate derivatives of **5** are based in part on the assignment of the acrylic acid derivative of **5** as the optically active form. Furthermore, the optically active diastereomer places the two CH(CO$_2$X) protons in a gauche disposition, and the associated small H–H coupling produces an effective ABC spin system and $^1H$ NMR spectra similar to that observed for the two-carbon-bridged complexes (Figure 6). In the meso isomer, the two CH(CO$_2$X) hydrogens have an anti arrangement and the relatively large H–H coupling ($\sim$7-8 Hz) results in features in the $^1H$ NMR associated with the actual AA′BB′CC′ spin system. Broadening and the appearance of additional structure on the meso -CH($CO_2X$) resonances relative to this peak in the optically active form are the most prominent observed differences. Computer simulation of the $^1H$ NMR spectra provides support for the isomer assignments (Figure 6). Efforts to establish the diastereomer assignments by using optically active shift reagents were unsuccessful, because steric demands of the ligands prohibit binding of shift reagents to the carboxylate group.

**Reactions of (TMP)Rh$^•$ and [(OEP)Rh]$_2$ with Methyl Methacrylate.** (Tetramesitylporphyrinato)rhodium(II), (TMP)Rh$^•$ (2), and [(OEP)Rh]$_2$ (1) react quantitatively with methyl methacrylate (MMA) to form alkenyl complexes and an equal quantity of a hydride and alkyl derivative, respectively (eqs 12 and 13). No evidence

$$2(TMP)Rh^{•} + CH_2{=}C(CH_3)(CO_2CH_3) \rightarrow (TMP)RhH + (TMP)RhCH_2C(CO_2CH_3){=}CH_2 \quad (12)$$

$$[(OEP)Rh]_2 + 2CH_2{=}C(CH_3)(CO_2CH_3) \rightarrow (OEP)RhCH_2CH(CH_3)(CO_2CH_3) + (OEP)RhCH_2C(CO_2CH_3){=}CH_2 \quad (13)$$

is obtained for either two- or four-carbon-bridged complexes in the reactions of MMA. Reaction 12 is several orders of magnitude faster than reaction 13 ($T \approx 295$ K), consistent with the need for dissociation of [(OEP)Rh]$_2$ ($D$(Rh–Rh) $\approx 16$ kcal mol$^{-1}$) to accomplish reaction 13.

The lack of observation of any two- or four-carbon-bridged complexes from reactions of methyl methacrylate contrasts with the acrylate $CH_2{=}CH(CO_2R)$ results. The absence of MMA bridging complexes (por)$RhCH_2C(CH_3)(CO_2CH_3)Rh$(por) results in part from steric hindrance to form a (por)Rh–tertiary carbon bond. Also, the presence of an accessible methyl CH group adjacent to the tertiary carbon center provides an optimum situation for H atom abstraction by (por)Rh$^•$ rather than collapse to an alkyl-bridged complex.

Reactions 12 and 13 are related to alkyl radical disproportionation ($2CH_3CH_2^{•} \rightleftharpoons CH_2{=}CH_2 + CH_3CH_3$) and are viewed as occurring through the intermediacy of metalloradical ((por)Rh$^•$) and metalloradical–alkene ([(por)$RhCH_2{=}C(CH_3)(CO_2CH_3)]^{•}$) complexes. Hydrogen atom abstraction by (por)Rh$^•$ from the methyl group of the intermediate alkene complex produces metal hydride, (por)RhH, and alkenyl, (por)$RhCH_2C(CO_2CH_3){=}CH_2$, complexes. Steric demands of the TMP ligand, which preclude dimerization of (TMP)Rh$^•$ through Rh–Rh bonding, apparently also inhibit reaction of the hydride with MMA to form (TMP)$RhCH_2CH(CH_3)(CO_2CH_3)$. Independent reactivity studies have demonstrated that (TMP)RhH fails to add with MMA at a finite rate under conditions where (OEP)RhH readily reacts with MMA to form (OEP)$RhCH_2CH(CH_3)(CO_2CH_3)$.

**Photoinduced (TMP)Rh-Catalyzed Polymerization of Acrylates.** The thermal dark reactions of (TMP)Rh$^•$ (2) with acrylates that occur at a finite rate are limited to formation of two- and four-carbon-bridged complexes. Single acrylate insertion results in derivatives of 4 that have strong (TMP)Rh–$CH_2$ bonds and weaker (TMP)Rh–CH($CO_2X$) bonds. Thermal homolytic dissociation of this weaker Rh–C bond provides a pathway to equilibrate the two- and four-carbon-bridged complexes and results exclusively in head to head C–C bond formation to produce (TMP)$RhCH_2CH(X)CH(X)CH_2Rh$(TMP) (5). Selective formation of the derivative of 5 that results from a head to head alkene dimerization is presumably driven by formation of two strong Rh–$CH_2$– bonds which are not capable of thermal bond homolysis at a finite rate at moderate temperatures.

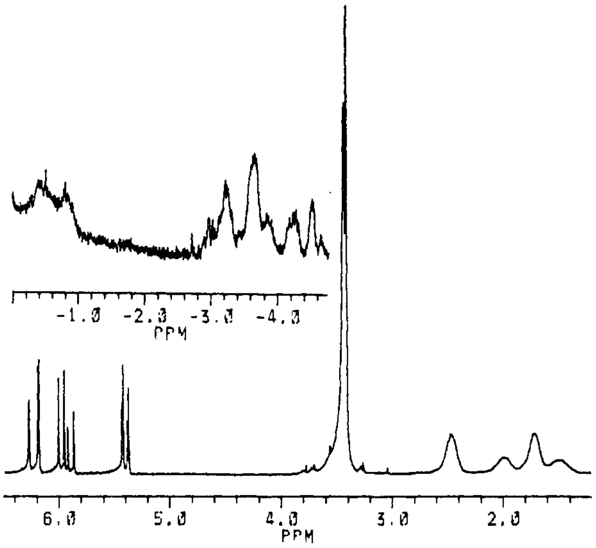


**Figure 7.** $^1H$ NMR (200 MHz) spectrum of atactic poly(methyl acrylate) formed in the photopromoted (TMP)Rh$^•$-catalyzed polymerization of methyl acrylate at an approximate conversion of 65% (300 K in $C_6D_6$).

Exposure of benzene solutions containing derivatives of 5 and large excesses of acrylates $CH_2{=}CH(CO_2X)$ (X = H, $CH_3$, $CH_2CH_3$) to visible light ($\lambda < 550$ nm) induces acrylate polymerization (Figure 7). The polymerization process stops when light is excluded and is reinitiated upon exposure to light. GPC measurements using refractive index and UV–vis ($\lambda = 420$ nm) detection manifest an increase in polymer molecular weight with increasing conversion up to 40–50% conversion and further show that (TMP)Rh units are attached to the polymer units. Attachment of the polymer unit to (TMP)Rh is also demonstrated by the high-field $^1H$ NMR resonances for the polymer attributed to the ring current effect of the porphyrin molecules on the acrylate units close to the site of metal bonding (Figure 7). FAB MS experiments of low conversion samples resulted in the detection of oligomer segments containing 1 (TMP)Rh unit with up to 15 methyl acrylate molecules. The (OEP)Rh system, which only forms two-carbon-bridged complexes with alkenes, is ineffective as a catalyst in the photopromoted polymerization of acrylates.

**Model for Reactions of Metalloradicals with Alkenes.** Conversion of ethene to the hypothetical diradical $^{•}CH_2CH_2^{•}$ requires approximately 64 kcal mol$^{-1}$, and reactions of ethene with radicals X$^•$ to form an alkyl radical ($XCH_2CH_2^{•}$) (eq 14) require the X–$CH_2$– bond dissociation

$$X^{•} + CH_2{=}CH_2 \rightarrow XCH_2CH_2^{•} \quad (14)$$

energy to exceed the sum of unfavorable entropy ($-T\Delta S^{\circ}_{14}$(298K) $\approx 8$ kcal mol$^{-1}$) and enthalpy ($\Delta H^{\circ}_{14} \approx 64$ kcal mol$^{-1}$) factors. Alkyl radicals readily react with alkenes to produce larger alkyl radicals because C–C bond formation is exothermic to the extent of ~85 kcal mol$^{-1}$, which more than compensates for loss of the C–C $\pi$ bond. This property gives alkyl radicals the capability to initiate and propagate radical polymerization of alkenes. Reactions of alkenes with metalloradicals have not yet been observed to produce carbon-centered metalloalkyl radicals or induce radical polymerization of alkenes. The currently known metal–alkyl bond dissociation energies are simply too small to fulfill the thermodynamic criteria for these processes.[15]

---

[15] Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

**Table I. Guidelines Estimates of Enthalpy Changes for Ethene Reactions Relevant to Metalloradical Activation of Alkenes[a,b]**

| | ~$\Delta H°$, kcal mol$^{-1}$ |
|---|---|
| $CH_2{=}CH_2 \rightleftharpoons {}^{\bullet}CH_2CH_2{}^{\bullet}$ | 64 |
| $2M^{\bullet} + CH_2{=}CH_2 \rightleftharpoons MCH_2CH_2M$ | $-2(M{-}CH_2{-}) + 64$ |
| $2M^{\bullet} + 2CH_2{=}CH_2 \rightleftharpoons M(CH_2)_4M$ | $-2(M{-}CH_2{-}) + 43$ |
| $M(CH_2)_2M + CH_2{=}CH_2 \rightleftharpoons M(CH_2)_4M$ | −21 |
| $M^{\bullet} + CH_2{=}CH_2 \rightleftharpoons MCH_2CH_2{}^{\bullet}$ | $M{-}CH_2{-} + 64$ |
| $MCH_2CH_2{}^{\bullet} \rightleftharpoons (MCH_2CH_2)^{\bullet}$ | relaxation enthalpy (RE) |
| $(MCH_2CH_2)^{\bullet} + CH_2{=}CH_2 \rightleftharpoons MCH_2CH_2CH_2CH_2{}^{\bullet}$ | −21 − RE |
| $2(MCH_2CH_2)^{\bullet} \rightleftharpoons M(CH_2)_4M$ | −85 − 2RE |
| $2MCH_2CH_2{}^{\bullet} \rightleftharpoons M(CH_2)_4M$ | −85 |
| $(por)Rh^{\bullet} + CH_2{=}CH_2 \rightleftharpoons (por)RhCH_2CH_2{}^{\bullet}$ | 14 |
| $(por)RhCH_2CH_2{}^{\bullet} \rightleftharpoons ((por)Rh(CH_2CH_2))^{\bullet}$ | −22 (RE) |
| $(por)Rh^{\bullet} + CH_2{=}CH_2 \rightleftharpoons ((por)Rh(CH_2CH_2))^{\bullet}$ | −8 |
| $((por)Rh(CH_2CH_2))^{\bullet} + CH_2{=}CH_2 \rightleftharpoons (por)RhCH_2CH_2CH_2CH_2{}^{\bullet}$ | +1 |
| $2((por)Rh(CH_2CH_2))^{\bullet} \rightarrow (por)RhCH_2(CH_2)_2CH_2Rh(por)$ | −41 |
| $(por)RhCH_2CH_2Rh(por) + CH_2{=}CH_2 \rightarrow (por)RhCH_2(CH_2)_2CH_2Rh(por)$ | −21 |

[a] Enthalpy changes for the generalized $M^{\bullet}$ reactions with ethene are estimated by using an ethene $\pi$ bond enthalpy of 64 kcal mol$^{-1}$ and a $CH_2{-}CH_2$ bond dissociation energy of 85 kcal mol$^{-1}$ (Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 6750. Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp 63–65. Parmar, S. S.; Benson, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 57. Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315). [b] The enthalpy values for $(por)RH^{\bullet}$ reactions are estimated using a $(por)Rh{-}CH_2{-}$ bond dissociation energy of 50 kcal mol$^{-1}$.[7]

Rhodium–alkyl bond energies achieve a maximum value in the methyl derivatives ($Rh{-}CH_3 \approx 58$ kcal mol$^{-1}$) and are substantially reduced in bonds with primary, secondary, and tertiary alkyl groups because of the increased steric requirements ($Rh{-}CH_2CH_2X \leq 50$ kcal mol$^{-1}$; $Rh{-}CH(CH_2X)_2 \leq 40$ kcal mol$^{-1}$).[7] Estimating the $Rh{-}CH_2CH_2{-}$ BDE as 50 kcal mol$^{-1}$ suggests that the reaction of $(por)Rh^{\bullet}$ with ethene to form a carbon-centered radical ($(por)RhCH_2CH_2{}^{\bullet}$) by eq 14 would be highly unfavorable ($\Delta H° \approx 14$ kcal mol$^{-1}$; $\Delta G°(298K) \approx 22$ kcal mol$^{-1}$) (Table I). The hypothetical localized carbon-centered radical $(por)RhCH_2CH_2{}^{\bullet}$ will be at higher energy than an alkene complex where there is only partial rehybridization, $[(por)Rh(CH_2CH_2)]^{\bullet}$ (eq 15). The difference in enthalpy

$$(por)Rh^{\bullet} + CH_2{=}CH_2 \rightarrow [(por)Rh(CH_2CH_2)]^{\bullet} \tag{15}$$

between the limiting alkyl radical formulation and the most stable complex is the relaxation enthalpy for the alkyl radical. In the case of rhodium porphyrins the relaxation enthalpy for $(por)RhCH_2CH_2{}^{\bullet}$ converting to the more stable metalloradical–alkene complex $[(por)Rh(CH_2CH_2)]^{\bullet}$ is estimated at ~−22 kcal mol$^{-1}$ (Table I). Complete rehybridization and reduction of the alkene occurs only when the metalloradical complex $[(por)Rh(CH_2CH_2)]^{\bullet}$ reacts with a second one-electron reagent ($X^{\bullet}$) capable of inducing the concerted formation of $X{-}CH_2$ and $Rh{-}CH_2$ normal covalent bonds.

[Tetrakis(2,4,6-triisopropylphenyl)porphyrinato]rhodium(II), $(TTiPP)Rh^{\bullet}$, forms a complex with ethene which on the basis of the EPR spectrum of the $^{13}C_2H_4$ derivative is assigned as a 1/1 metalloradical ethene $\pi$ complex.[16] Also an intermediate with 1/1 stoichiometry of $(OEP)Rh^{\bullet}$ and styrene, $[(OEP)Rh(CH_2CH(C_6H_5))]^{\bullet}$, has been kinetically implicated in radical-like chain reactions of $[(OEP)Rh]_2$,[3] and related species are probable central intermediates in rhodium(II) porphyrin reactions with acrylates. It is easy to envision how $[(por)Rh(CH_2{=}CH(X))]^{\bullet}$ species could function as productive intermediates in the formation of two- and four-carbon-bridged complexes (eqs 16 and 17) as well as several pathways for disproportionation (eqs 18–20). Each of these reactions

$$[(por)Rh(CH_2{=}CH(X))]^{\bullet} + (por)Rh^{\bullet} \rightarrow (por)RhCH_2CH(X)Rh(por) \tag{16}$$

$$2[(por)Rh(CH_2{=}CH(X))]^{\bullet} \rightarrow (por)RhCH_2CH(X)CH(X)CH_2Rh(OEP) \tag{17}$$

$$2[(por)Rh(CH_2{=}C(CH_3)(X))]^{\bullet} \rightarrow (por)RhCH_2C(X){=}CH_2 + (por)RhCH_2CH(CH_3)(X) \tag{18}$$

$$[(por)Rh(CH_2{=}C(CH_3)(X))]^{\bullet} + (por)Rh^{\bullet} \rightarrow (por)RhH + (por)RhCH_2C(X){=}CH_2 \tag{19}$$

$$[(por)Rh(CH_2{=}C(CH_3)(X))]^{\bullet} + (por)RhH \rightarrow (por)RhCH_2CH(CH_3)(X) + (por)Rh^{\bullet} \tag{20}$$

has an analog in alkyl radical reactions with alkenes,[17] but an important difference is that a single $(por)Rh^{\bullet}$ is incapable of reacting with an alkene to form an authentic carbon-centered radical. This further implies that $(por)Rh^{\bullet}$ species cannot directly initiate radical polymerization of alkenes.

Reaction of the two-carbon-bridged complex with ethene to produce a four-carbon-bridged species (eq 21) is ther-

$$MCH_2CH_2M + CH_2{=}CH_2 \rightleftharpoons MCH_2(CH_2)_2CH_2M \tag{21}$$

modynamically highly favorable ($\Delta H° \approx -21$ kcal mol$^{-1}$; $\Delta G°(298K) \approx -13$ kcal mol$^{-1}$) (Table I), and this chain lengthening process should be favorable for all alkenes. $[(OEP)Rh]_2$ reacts with acrylates to form only two-carbon-alkyl-bridged complexes $(OEP)RhCH_2CH(X)Rh(OEP)$ ($X = CO_2H, CO_2CH_3, CO_2C_2H_5$) at a finite rate. Subsequent insertions of $CH_2{=}CH(X)$ into one of the Rh—C bonds to produce four-carbon-alkyl-bridged complexes must be thermodynamically favorable, and so the absence of observed multiple insertions is kinetic in origin. $(OEP)Rh{-}CH_2{-}$ and $(OEP)Rh{-}CH(X){-}$ bond energies are approximately 50 and 40 kcal mol$^{-1}$, respectively,[7] and these values are too large to yield thermal bond homolysis with a finite rate at moderate temperatures.

Increased steric demands of TMP produce unfavorable interaction between each TMP and the bridging alkyl group and also between the two TMP groups that are held relatively close together by the bridging alkyl units. These unfavorable steric interactions reduce the effective Rh–C bond dissociation energy which provides a lower activation energy pathway for bond homolysis (eq 22) and subsequent

$$(TMP)RhCH_2CH(X)Rh(TMP) \rightleftharpoons (TMP)Rh^{\bullet} + [(TMP)Rh(CH_2CH(X))]^{\bullet} \tag{22}$$

formation of the thermodynamically favored four-carbon-bridged complex. Selective formation of the head to head four-carbon bridging alkyl unit without any further alkene oligomerization suggests that either the acrylate inserts into a geminate radical pair ($[(TMP)Rh(CH_2CH(X))]^{\bullet}, {}^{\bullet}Rh(TMP)$) or two $[(TMP)Rh(CH_2CH(X))]^{\bullet}$ groups

---

(16) Formation of metalloradical–alkene $\pi$ complex at low temperatures in the reaction of [tetrakis(1,3,5-triisopropylphenyl)porphyrinato]rhodium(II) with ethene has been observed by EPR spectroscopy. Bunn, A. G.; Wayland, B. B. *J. Am. Chem. Soc.* **1992**, *114*, 6917.

(17) Odian, G. G. *Principles of Polymerization*, 2nd ed.; Wiley-Interscience: New York, 1981.

couple. A pathway that involves reaction of [(TMP)Rh(CH$_2$CH(X))]$^•$ with a second acrylate to form a carbon-centered radical would be expected to produce head to tail alkene dimerization, (TMP)RhCH$_2$CH(X)CH$_2\dot{C}$H(X), and further oligomerization, which are inconsistent with the experimental observations.

Photoinduced polymerization of acrylates is observed only for the (TMP)Rh system. We believe that photolysis of the two-carbon-bridged complexes is ineffective in initiating polymerization and that only systems where thermal reactions produce four-carbon or larger alkyl bridges will be effective. Photohomolysis of a Rh–C bond in the two-carbon-bridged species results in Rh$^•$ and (Rh(CH$_2$CH(X)))$^•$. The alkene complex Rh(CH$_2$CH(X))$^•$ is not an authentic alkyl radical and cannot initiate alkene polymerization. Photolysis of a four-carbon-bridged complex results in Rh–C bond homolysis to yield Rh$^•$ and a carbon-based radical, RhCH$_2$CH(X)CH(X)CH$_2{}^•$ (eq 23), which can initiate alkene polymerization (eq 24). Polymerization is terminated by capping with (por)Rh$^•$ or coupling with another growing polymer radical. The resulting polymer retains terminal (por)Rh units which can be used to photoinitiate further polymerization and give "living" character to the system, but continual regeneration of the initiator from (TMP)Rh$^•$ results in broader molecular weight distributions than those associated with authentic living polymerization processes.

$$\mathrm{RhCH_2CH(X)CH(X)CH_2Rh} \xrightarrow{h\nu} \mathrm{RhCH_2CH(X)CH(X)CH_2{}^{\bullet}} + \mathrm{Rh}^{\bullet} \quad (23)$$

$$\mathrm{RhCH_2CH(X)CH(X)CH_2{}^{\bullet}} + n\mathrm{CH_2{=}CH(X)} \rightarrow \mathrm{RhCH_2CH(X)CH(X)CH_2(CH_2CH(X))_{\mathit{n}-1}CH_2\dot{C}H(X)} \quad (24)$$

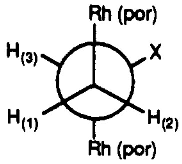
## Experimental Section

**General Methods.** All manipulations were performed by vacuum line techniques. NMR data were recorded on either IBM-Bruker WP 200SY or Bruker Instruments AF500SY at ambient temperature. Mass spectrometry results were obtained on a VG ZAB-E mass spectrometer using the fast-atom bombardment (FAB) method. Polymer samples were analyzed on a Hewlett-Packard 1090 liquid chromatograph. Structure simulations were performed with the Chem 3D Plus 3.0 molecular modeling program licensed from Cambridge Scientific Computing Inc. NMR spectra were simulated by using NMR$^{\mathrm{II}}$ Version 1.0 software licensed from Calleo Scientific Software Publishers. The stoichiometry and structures of reaction products in solution were assigned by use of $^1$H NMR and FAB mass spectra. Microanalytical data could not be obtained due to the small quantities of materials available.

**Solvents.** Benzene was degassed by freeze–pump–thaw cycles and then refluxed over sodium/benzophenone until the indicator turned purple.

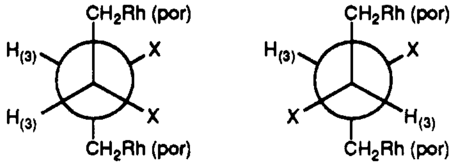
**Reagents.** Styrene, 3-methylstyrene, and methyl methacrylate were purchased from Aldrich. Acrylates containing 20–200 ppm of hydroquinone monomethyl ether as a polymerization inhibitor were received as a donation from du Pont Marshall Laboratories. Separation of the alkenes from the inhibitor was achieved by chromatography on grade I basic alumina and by vacuum transfer of the more volatile alkene away from the substantially less volatile inhibitor. [Rh(CO)$_2$Cl]$_2$ and octaethylporphyrin ((OEP)H$_2$) were used as purchased from Aldrich. ((TMP)H$_2$) was prepared by the method of Lindsey.[18] [(OEP)Rh]$_2$ and (TMP)RhCH$_3$ were prepared by literature methods.[2,4]

**$^1$H NMR Notations for Two- and Four-Carbon-Alkyl-Bridged Complexes. (por)RhCH$_2$CHXRh(por).** H$_{(1)}$ and H$_{(2)}$ are geminal hydrogens, and H$_{(3)}$ is geminal to the X group. H$_{(2)}$ and H$_{(3)}$ are in an anti ("trans") position, and H$_{(1)}$ and H$_{(3)}$ are in a gauche ("cis") position relative to each other.



X = CO$_2$H, CO$_2$CH$_3$, CO$_2$CH$_2$CH$_3$, C$_6$H$_5$, C$_6$H$_4$CH$_3$

**(por)RhCH$_2$CHXCHXCH$_2$Rh(por).** In bridged (TMP)Rh complexes each mesityl group has one set of ortho methyl groups and meta hydrogens that point inward toward the second porphyrin ($o$-CH$_{3(\mathrm{in})}$, $m$-H$_{(\mathrm{in})}$) and one set that is directed outward from the opposite porphyrin ($o$-CH$_{3(\mathrm{out})}$, $m$-H$_{(\mathrm{out})}$).



optically active (*rr,ss*)　　meso (*rs,sr*)

X = CO$_2$H, CO$_2$CH$_3$, CO$_2$CH$_2$CH$_3$

**Reactions of [(OEP)Rh]$_2$.** A general procedure was used in examining the reactions of [(OEP)Rh]$_2$ with CH$_2$=CH(X) (X = CO$_2$H, CO$_2$CH$_3$, CO$_2$CH$_2$CH$_3$, C$_6$H$_5$, C$_6$H$_4$CH$_3$) and CH$_2$=C(CH$_3$)(CO$_2$CH$_3$). Weighted samples of [(OEP)Rh]$_2$ (~0.5 mg) were placed into vacuum-adapted NMR tubes, followed by evacuation and sequential vacuum transfer of deuterated benzene as solvent (~0.5 mL) and variable quantities of an alkene (0.1–5.0 mg). The NMR tubes were subsequently sealed, and $^1$H NMR was used in following the evolution of reaction products ($T$ = 300 K).

**Reactions of [(OEP)Rh]$_2$ with Acrylates.** The $^1$H NMR for each of the complexes formed indicated the presence of two inequivalent porphyrin units, and integration showed that the reaction products have the stoichiometry of two (OEP)Rh units per acrylate. Observation of three high-field multiplets ($\delta$ ~−9 to −12 ppm) each corresponding to a single hydrogen with $^{103}$Rh coupling ($^2J_{103,\mathrm{RhH}} \approx$ 2–3 Hz) is characteristic of –CH$_2$CH(X)– units bridging two rhodium porphyrins which shows that each of the complexes has the same type of structural formula, (OEP)RhCH$_2$CH(CO$_2$X)Rh(OEP) (X = H, CH$_3$, CH$_2$CH$_3$). The presence of a chiral carbon center in the bridging alkyl group is manifested by inequivalence of the CH$_2$ hydrogens in the bridge and the adjacent ethyl groups on each pyrrole (Figure 1).

**(OEP)RhCH$_2$CH(CO$_2$H)Rh(OEP).** $^1$H NMR (C$_6$D$_6$): $\delta$ 9.39 (s, 4 H, porphyrin —CH=), 9.37 (s, 4 H, porphyrin —CH=), 4.02, 3.96, 3.89, 3.77 (overlapping m, 32 H, C$H_2$CH$_3$), 1.80, 1.78, 1.75, 1.74 (overlapping t, 48 H, CH$_2$C$H_3$), −10.14 (m, 1 H, CH$_{(1)}H_{(2)}$CH$_{(3)}$COOH), −10.39 (m, 1 H, CH$_{(1)}$H$_{(2)}$C$H_{(3)}$COOH), −12.12 (m, 1 H, C$H_{(1)}$H$_{(2)}$CH$_{(3)}$COOH); $^2J_{\mathrm{H(1)H(2)}}$ = 7.0 Hz, $^3J_{\mathrm{H(1)H(3)}}$ = 3.1 Hz, $^3J_{\mathrm{H(2)H(3)}}$ = 12.1 Hz, $^2J_{103,\mathrm{RhH(1)}} \approx {}^2J_{103,\mathrm{RhH(2)}} \approx {}^2J_{103,\mathrm{RhH(3)}} \approx$ 3 Hz. FAB MS: $m/e$ 1342.

**(OEP)RhCH$_2$CH(CO$_2$CH$_3$)Rh(OEP).** Reaction of [(OEP)Rh]$_2$ with methyl acrylate results in formation of two isomers of (OEP)RhCH$_2$CH(CO$_2$CH$_3$)Rh(OEP) in equal amounts. The two sets of high-field resonances for the –CH$_2$CH(CO$_2$CH$_3$)– bridging alkyl are readily assigned by proton decoupling experiments, but occurrence of equal amounts of the two isomers precluded associating the porphyrin resonances with a particular set of bridging alkyl peaks. $^1$H NMR (in C$_6$D$_6$) of isomer A: $\delta$ −9.82 (m, 1 H, CH$_{(1)}H_{(2)}$CH$_{(3)}$CO$_2$CH$_3$), −10.20 (m, 1 H, CH$_{(1)}$H$_{(2)}$C$H_{(3)}$CO$_2$CH$_3$), −12.09 (m, 1 H, C$H_{(1)}$H$_{(2)}$CH$_{(3)}$CO$_2$CH$_3$); $^2J_{\mathrm{H(1)H(2)}}$ = 6.5 Hz, $^3J_{\mathrm{H(1)H(3)}}$ = 3.0 Hz, $^3J_{\mathrm{H(2)H(3)}}$ = 12.0 Hz, $^2J_{103,\mathrm{RhH(1)}} \approx {}^2J_{103,\mathrm{RhH(2)}} \approx {}^2J_{103,\mathrm{RhH(3)}} \approx$ 3 Hz. $^1$H NMR (C$_6$D$_6$) of isomer B: $\delta$ −10.02 (m, 1 H, CH$_{(1)}H_{(2)}$CH$_{(3)}$CO$_2$CH$_3$), −10.35 (m, 1 H, CH$_{(1)}$H$_{(2)}$C$H_{(3)}$CO$_2$CH$_3$), −12.09 (m, 1 H, C$H_{(1)}$H$_{(2)}$CH$_{(3)}$CO$_2$CH$_3$); $^2J_{\mathrm{H(1)H(2)}}$ = 6.5 Hz, $^3J_{\mathrm{H(1)H(3)}}$ = 3.0 Hz, $^3J_{\mathrm{H(2)H(3)}}$ = 12.0 Hz, $^2J_{103,\mathrm{RhH(1)}} \approx {}^2J_{103,\mathrm{RhH(2)}} \approx {}^2J_{103,\mathrm{RhH(3)}} \approx$ 3 Hz. $^1$H NMR (C$_6$D$_6$) of isomers A and B: $\delta$ 9.38 (s, 4 H, porphyrin —CH=), 9.37 (s, 4 H, porphyrin —CH=), 9.35 (s, 4 H, porphyrin —CH=), 9.31 (s, 4 H, porphyrin —CH=), 3.96–3.74 (overlapping m, 2 × 32 H, C$H_2$CH$_3$), 1.79–1.73 (overlapping t, 2

---

[18] Wagner, R. W.; Laurence, D. S.; Lindsey, J. S. *Tetrahedron Lett.* 1987, *28*, 3029.

× 48 H, $CH_2CH_3$), 1.09 (s, 3 H, $CO_2CH_3$), 0.57 (s, 3 H, $CO_2CH_3$). FAB MS: *m/e* 1356.

**$(OEP)RhCH_2CH(CO_2CH_2CH_3)Rh(OEP)$.** Reaction of $[(OEP)Rh]_2$ with ethyl acrylate produces two isomers of $(OEP)RhCH_2CH(CO_2CH_2CH_3)Rh(OEP)$ in an A to B ratio of 1/2 so that the complete $^1H$ NMR for each isomer can be assigned. $^1H$ NMR ($C_6D_6$) of isomer A: $\delta$ 9.34 (s, 4 H, porphyrin —CH═), 9.28 (s, 4 H, porphyrin —CH═), 3.99, 3.82 (overlapping m, 32 H, porphyrin $CH_2CH_3$), 1.82, 1.75 (overlapping t, 48 H, porphyrin $CH_2CH_3$), 0.57 (t, 3 H, $CO_2CH_2CH_3$), −9.93 (m, 1 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2Et$), −10.12 (m, 1 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2Et$), −12.01 (m, 1 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2Et$); $^2J_{H_{(1)}H_{(2)}} = 7.0$ Hz, $^3J_{H_{(1)}H_{(3)}} = 3.0$ Hz, $^3J_{H_{(2)}H_{(3)}} = 12.5$ Hz, $^2J_{103,RhH_{(1)}} \approx {^2J_{103,RhH_{(2)}}} \approx {^2J_{103,RhH_{(3)}}} \approx 3$ Hz. $^1H$ NMR ($C_6D_6$) of isomer B: $\delta$ 9.35 (s, 4 H, porphyrin —CH═), 9.32 (s, 4 H, porphyrin —CH═), 3.99, 3.74 (overlapping m, 32 H, porphyrin $CH_2CH_3$), 1.75, 1.74 (overlapping t, 48 H, porphyrin $CH_2CH_3$), −0.19 (t, 3 H, $CO_2CH_2CH_3$), −9.93 (m, 1, H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2Et$), −10.42 (m, 1 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2Et$), −12.06 (m, 1 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2Et$); $^2J_{H_{(1)}H_{(2)}} = 7.0$ Hz, $^3J_{H_{(1)}H_{(3)}} = 3.0$ Hz, $^3J_{H_{(2)}H_{(3)}} = 12.5$ Hz, $^2J_{103,RhH_{(1)}} \approx {^2J_{103,RhH_{(2)}}} \approx {^2J_{103,RhH_{(3)}}} \approx 3$ Hz. The $CO_2CH_2CH_3$ resonances are obscured by other peaks for both isomers. FAB MS: *m/e* 1370.

**Reaction of $[(OEP)Rh]_2$ with Methyl Methacrylate.** $[(OEP)Rh]_2$ reacts quantitatively with methyl methacrylate to form exclusively $(OEP)RhCH_2CH(CH_3)(CO_2CH_3)$ and $(OEP)RhCH_2C(CO_2CH_3){=}CH_2$ in equal quantities over a period of 2 days at 300 K.

**$(OEP)RhCH_2CH(CH_3)(CO_2CH_3)$.** $^1H$ NMR ($C_6D_6$): $\delta$ 10.21 (s, 4 H, porphyrin —CH═), 4.01–3.94 (m, 16 H, porphyrin $CH_2CH_3$), 2.35 (s, 3 H, $-CO_2CH_3$), 1.92–1.90 (dt, 24 H, porphyrin $CH_2CH_3$), −1.99 (d, 3 H, $-CH(CH_3)(CO_2CH_3)$, $^3J_{HH} = 7.2$ Hz), −4.19 (m, 1 H, $-CH(CH_3)(CH_3)(CO_2CH_3)$), −4.56 (ddd, 1 H, $RhCH_{(1)}H_{(2)}-$, $^2J_{HH} = 8.0$ Hz, $^3J_{HH} = 8.0$ Hz, $^2J_{103,RhH} = 3.0$ Hz), −5.45 (ddd, 1 H, $RhCH_{(1)}H_{(2)}-$, $^2J_{HH} = 8.0$ Hz, $^3J_{HH} = 3.5$ Hz, $^2J_{103,RhH} = 3.5$ Hz). FAB MS: *m/e* 736. The presence of an optically active carbon center in the complex is manifested by inequivalence of the two $RhCH_2-$ proton resonances and the adjacent ethyl groups on each pyrrole.

**$(OEP)RhCH_2C(CO_2CH_3){=}CH_2$.** $^1H$ NMR ($C_6D_6$): $\delta$ 10.18 (s, 4 H, porphyrin —CH═), 3.98 (m, 16 H, porphyrin $CH_2CH_3$), 2.46 (s, 3 H, $-CO_2CH_3$), 1.91 (t, 24 H, porphyrin $CH_2CH_3$), −4.26 (d, 2 H, $RhCH_2-$, $^2J_{103,RhH} = 3.6$ Hz). The ═$CH_2$ resonances are obscured by other peaks. FAB MS: *m/e* 734.

**Reactions of $[(OEP)Rh]_2$ with Styrene and 3-Methylstyrene.** The reactions of $[(OEP)Rh]_2$ with styrene and 3-methylstyrene reached completion by the time the first NMR spectra were recorded. The $^1H$ NMR spectrum of $(OEP)RhCH_2CH(C_6H_5)Rh(OEP)$ has been previously reported by Halpern and co-workers.[3]

**$(OEP)RhCH_2CH(C_6H_5)Rh(OEP)$.** $^1H$ NMR ($C_6D_6$): $\delta$ 9.22 (s, 4 H, porphyrin —CH═), 9.18 (s, 4 H, porphyrin —CH═), 6.24 (dd, 1 H, para H), 5.49 (dd, 1 H, meta H), 5.00 (dd, 1 H, meta H), 3.94–3.76 (overlapping m, 32 H, $CH_2CH_3$), 1.77 (overlapping t, 48 H, $CH_2CH_3$), 0.55 (d, 1 H, ortho H), −0.79 (d, 1 H, ortho H), −8.94 (m, 1 H, $-CH_{(1)}H_{(2)}CH_{(3)}(C_6H_5)-$), −9.90 (m, 1 H, $-CH_{(1)}H_{(2)}CH_{(3)}(C_6H_5)-$), −11.33 (m, 1 H, $-CH_{(1)}H_{(2)}CH_{(3)}(C_6H_5)-$); $^2J_{H_{(1)}H_{(2)}} = 7.8$ Hz, $^3J_{H_{(1)}H_{(3)}} \approx 1\text{–}2$ Hz, $^3J_{H_{(2)}H_{(3)}} = 12.0$ Hz, $^2J_{103,RhH_{(1)}} \approx {^2J_{103,RhH_{(2)}}} \approx {^2J_{103,RhH_{(3)}}} \approx 2$ Hz; for all $C_6H_5$ hydrogens, $^3J_{HH} = 7.5$ Hz. FAB MS: *m/e* 1374.

The reaction of $[(OEP)Rh]_2$ with 3-methylstyrene results in the formation of two isomers of $(OEP)RhCH_2CH(C_6H_4CH_3)Rh(OEP)$. The formation of equal amounts of the isomers precluded associating the porphyrin resonances with a particular set of bridging alkyl peaks or a set of phenyl hydrogen resonances.

**$(OEP)RhCH_2CH(C_6H_4CH_3)Rh(OEP)$.** $^1H$ NMR ($C_6D_6$): $\delta$ 9.23 (br, 8 H, porphyrin —CH═), 9.19 (br, 8 H, porphyrin —CH═), 6.06 (d, 1 H, para H), 6.05 (d, 1 H, para H), 5.40 (dd, 1 H, meta H), 4.93 (dd, 1 H, meta H), 3.95–3.74 (overlapping m, 2 × 32 H, $CH_2CH_3$), 1.75 (overlapping t, 2 × 48 H, $CH_2CH_3$), 1.88 (s, 3 H, $-C_6H_4CH_3$), 1.46 (s, 3 H, $-C_6H_4CH_3$), 0.40 (d, 1 H, ortho H), 0.25 (s, 1 H, ortho H), −0.95 (d, 1 H, ortho H), −1.03 (s, 1 H, ortho H), −8.93 (overlapping m, 2 H, $-CH_{(1)}H_{(2)}CH_{(3)}(C_6H_4CH_3)$), −9.80 (m, 1 H, $-CH_{(1)}H_{(2)}CH_{(3)}(C_6H_4CH_3)$), −9.89 (m, 1 H, $-CH_{(1)}H_{(2)}CH_{(3)}(C_6H_4CH_3)$), −11.33 (overlapping m, 2 H, $-CH_{(1)}H_{(2)}CH_{(3)}(C_6H_4CH_3)$); $^2J_{H_{(1)}H_{(2)}} = 7.8$ Hz, $^3J_{H_{(1)}H_{(3)}} = 1\text{–}2$ Hz, $^3J_{H_{(2)}H_{(3)}} = 12.0$ Hz, $^2J_{103,RhH_{(1)}} \approx {^2J_{103,RhH_{(2)}}} \approx {^2J_{103,RhH_{(3)}}} \approx 2$ Hz; for all phenyl hydrogens, $^3J_{HH} = 7.5$ Hz. FAB MS: *m/e* 1388.

**Reactions of (TMP)Rh.** Weighed samples of $(TMP)RhCH_3$ (~0.5 mg) were placed in vacuum-adapted NMR tubes and evacuated prior to vacuum transfer of benzene (~0.5 mL) as solvent. The solution was photolyzed for 6 h in a Rayonnet photoreactor ($\lambda \geq 350$ nm) which is known to result in the complete conversion of $(TMP)RhCH_3$ to $(TMP)Rh^•$.[2] The benzene solution of $(TMP)Rh^•$ was evacuated to dryness followed by sequential vacuum transfer of $C_6D_6$ (~0.5 mL) and varying quantities of an alkene.

**Reactions of $(TMP)Rh^•$ with Acrylates $CH_2{=}CH(CO_2X)$ (X = H, $CH_3$, $CH_2CH_3$).** Evolution of the reaction products was followed by $^1H$ NMR. Sets of bridging alkyl hydrogen resonances were assigned by decoupling experiments and associated with porphyrin $^1H$ resonances by the relative intensities. Integration of the $^1H$ NMR showed that the products either had a stoichiometry of two (TMP)Rh per acrylate or one (TMP)Rh per acrylate which on the basis of $^1H$ NMR were assigned structures containing two- and four-carbon units bridging two (TMP)Rh groups. The four-carbon-alkyl-bridged complexes invariably contain two chemically equivalent (TMP)Rh units and three types of chemically inequivalent bridging alkyl hydrogens with relative intensity of 2. These features indicate the presence of a symmetrical bridging alkyl unit that results from head to head alkene dimerization, $(TMP)RhCH_2CH(X)CH(X)CH_2Rh(TMP)$. The presence of chiral carbon centers in the alkyl-bridged complexes is manifested in the $^1H$ NMR by inequivalence of the bridging alkyl $CH_2$ hydrogens and the adjacent hydrogens on the pyrrole units. Two chiral centers in the four-carbon-bridged complexes result in diastereomers which are observed for the methyl and ethyl acrylate derivatives, but only one of the two diastereomers is observed for the acrylic acid derivative (Figures 3 and 4).

**Reactions of $(TMP)Rh^•$ with $CH_2{=}CH(CO_2CH_3)$.** Transferring $CH_2{=}CH(CO_2CH_3)$ into a $C_6D_6$ solution of $(TMP)Rh^•$ to produce a mole ratio greater than 1/1 results in the immediate disappearance of $(TMP)Rh^•$ with formation of $(TMP)RhCH_2CH(CO_2CH_3)Rh(TMP)$ and a small quantity of two isomers of $(TMP)RhCH_2CH(CO_2CH_3)CH(CO_2CH_3)CH_2Rh(TMP)$ (< 5 mol %). A slow subsequent reaction which occurs in a period of hours to days dependent on the acrylate to (TMP)Rh mole ratio results in the quantitative formation of equal amounts of two diastereomers of $(TMP)RhCH_2CH(CO_2CH_3)CH(CO_2CH_3)CH_2Rh(TMP)$. The optically active diastereomer with the two $-CH_2Rh(TMP)$ groups in anti positions places the two interior $CH(H_{(3)})$ hydrogens in guache positions where $J_{H_{(3)}H_{(3')}}$ is small (<2 Hz) which results in the bridging alkyl hydrogens appearing as an effective ABC $^1H$ NMR pattern. The interior CH hydrogens in the meso isomer are in anti positions where effects of the large $J_{H_{(3)}H_{(3')}}$ (~7–8 Hz) are manifested in the $^1H$ NMR. Simulations of the $^1H$ NMR for the bridging alkyl hydrogens were used in assigning isomer B to the meso and isomer A to the optically active diastereomer. Placing the solution containing equal amounts of these diastereomers in a Rayonnet photoreactor and photolyzing for 1 h resulted in the preferential photolysis of the meso isomer, thus permitting assignment of the porphyrin $^1H$ NMR resonances for each diastereomer.

**$(TMP)RhCH_2CH(CO_2CH_3)Rh(TMP)$.** $^1H$ NMR ($C_6D_6$): $\delta$ 8.272 (d, 4 H, pyrrole, $^3J_{HH} = 4.8$ Hz), 8.262 (d, 4 H, pyrrole, $^3J_{HH} = 4.8$ Hz), 8.233 (d, 4 H, pyrrole, $^3J_{HH} = 4.8$ Hz), 8.231 (d, 4 H, pyrrole, $^3J_{HH} = 4.8$ Hz), 7.30 (s, 4 H, mesityl meta $H_{(out)}$), 7.29 (s, 4 H, mesityl meta $H_{(out)}$), 6.85 (s, 4 H, mesityl meta $H_{(in)}$), 6.81 (s, 4 H, mesityl meta $H_{(in)}$), 2.46 (s, 12 H, mesityl ortho $CH_{3(out)}$), 2.41 (s, 12 H, mesityl para $CH_3$), 2.40 (s, 12 H, mesityl para $CH_3$), 2.37 (s, 12 H, mesityl ortho $CH_{3(out)}$), 1.53 (s, 3 H, $CO_2CH_3$), 0.83 (s, 12 H, mesityl ortho $CH_{3(in)}$), 0.65 (s, 12 H, mesityl ortho $CH_{3(in)}$), −5.41 (m, 1 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2CH_3$), −6.21 (m, 1 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2CH_3$), −7.01 (s, 1 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2CH_3$); $^2J_{H_{(1)}H_{(2)}} = 3.6$ Hz, $^3J_{H_{(1)}H_{(3)}} = 3.5$ Hz, $^3J_{H_{(2)}H_{(3)}} = 12.5$ Hz, $^2J_{103,RhH_{(1)}} \cong {^2J_{103,RhH_{(2)}}} \cong {^2J_{103,RhH_{(3)}}} \cong 3$ Hz. FAB MS: *m/e* 1852.

**$(TMP)RhCH_2CH(CO_2CH_3)CH(CO_2CH_3)CH_2Rh(TMP)$.** $^1H$ NMR ($C_6D_6$) of isomer A: $\delta$ 8.42 (d, 8 H, pyrrole, $^3J_{HH} = 4.6$ Hz), 8.36 (d, 8 H, pyrrole, $^3J_{HH} = 4.6$ Hz), 7.29 (s, 8 H, mesityl meta $H_{(out)}$), 6.99 (s, 8 H, mesityl meta $H_{(in)}$), 2.44 (s, 24 H, mesityl para $CH_3$), 2.18 (s, 6 H, $CO_2CH_3$), 1.98 (s, 24 H, mesityl ortho $CH_{3(out)}$), 1.45 (s, 24 H, mesityl ortho $CH_{3(in)}$), −5.15 (d, 2 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2CH_3$), −5.68 (m, 2 H, $CH_{(1)}H_{(2)}CH_{(3)}CO_2CH_3$), −6.75 (m, 2 H, $\mathrm{C}\mathit{H}_{(1)}\mathrm{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2CH_3}$); $^2J_{\mathrm{H}_{(1)}\mathrm{H}_{(2)}} = 8.3$ Hz, $^3J_{\mathrm{H}_{(1)}\mathrm{H}_{(3)}} \approx 1$–2 Hz, $^3J_{\mathrm{H}_{(2)}\mathrm{H}_{(3)}} = 11.0$ Hz, $^2J_{103,\mathrm{RhH}_{(1)}} \cong {}^2J_{103,\mathrm{RhH}_{(2)}} \cong 2.5$ Hz, $^3J_{103,\mathrm{RhH}_{(3)}} \approx 0$ Hz. $^1$H NMR ($C_6D_6$) of isomer B: $\delta$ 8.43 (d, 8 H, pyrrole, $^3J_{\mathrm{HH}} = 4.7$ Hz), 8.41 (d, 8 H, pyrrole, $^3J_{\mathrm{HH}} = 4.7$ Hz), 7.23 (s, 8 H, mesityl meta $\mathrm{H}_{(\mathrm{out})}$), 6.99 (s, 8 H, mesityl meta $\mathrm{H}_{(\mathrm{in})}$), 2.41 (s, 24 H, mesityl para $CH_3$), 1.95 (s, 24 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{out})}$), 1.69 (s, 6 H, $CO_2CH_3$), 1.47 (s, 24 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{in})}$), −4.91 (m, 2 H, $\mathrm{CH}_{(1)}\mathit{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2CH_3}$), −5.22 (d, 2 H, $\mathrm{CH}_{(1)}\mathrm{H}_{(2)}\mathrm{C}\mathit{H}_{(3)}\mathrm{CO_2CH_3}$), −5.97 (m, 2 H, $\mathrm{C}\mathit{H}_{(1)}\mathrm{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2CH_3}$); $^2J_{\mathrm{H}_{(1)}\mathrm{H}_{(2)}} = 6.5$ Hz, $^3J_{\mathrm{H}_{(1)}\mathrm{H}_{(3)}} \approx 1$–2 Hz, $^3J_{\mathrm{H}_{(2)}\mathrm{H}_{(3)}} = 10.1$ Hz, $^2J_{103,\mathrm{RhH}_{(1)}} \cong {}^2J_{103,\mathrm{RhH}_{(2)}} \cong 2.8$ Hz, $^3J_{103,\mathrm{RhH}_{(3)}} \approx 0$ Hz. FAB MS: *m/e* 1938.

**Reactions of (TMP)Rh$^\bullet$ with $CH_2{=}CH(CO_2CH_2CH_3)$.** Reaction of ethyl acrylate with (TMP)Rh$^\bullet$ in mole ratios varying from 0.3 to 10 produces two diastereomers of (TMP)$RhCH_2CH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)CH_2Rh$(TMP) in a 2/1 ratio as the exclusive $^1$H NMR observable products. No evidence was found for a two-carbon-bridged complex even at the smallest mole ratio where equilibrium between (TMP)Rh$^\bullet$, $CH_2{=}CH(CO_2CH_2CH_3)$, and the four-carbon-bridged complexes is observed. The majority diastereomer (A) is assigned as the enantiomeric pair on the basis of the similarity of its $^1$H NMR spectrum to that of the methyl acrylate enantiomeric pair, and the minority diastereomer (B) is assigned as the meso form. $^1$H NMR ($C_6D_6$) of isomer A: $\delta$ 8.42 (d, 8 H, pyrrole, $^3J_{\mathrm{HH}} = 4.6$ Hz), 8.36 (d, 8 H, pyrrole, $^3J_{\mathrm{HH}} = 4.6$ Hz), 7.30 (s, 8 H, mesityl meta $\mathrm{H}_{(\mathrm{out})}$), 6.99 (s, 8 H, mesityl meta $\mathrm{H}_{(\mathrm{in})}$), 2.44 (s, 24 H, mesityl para $CH_3$), 2.01 (s, 24 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{out})}$), 1.44 (s, 24 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{in})}$), 0.66 (t, 6 H, $\mathrm{CO_2CH_2C}\mathit{H}_3$), −4.94 (d, 2 H, $\mathrm{CH}_{(1)}\mathrm{H}_{(2)}\mathrm{C}\mathit{H}_{(3)}\mathrm{CO_2CH_2CH_3}$), −5.60 (m, 2 H, $\mathrm{CH}_{(1)}\mathit{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2CH_2CH_3}$), −6.72 (m, 2 H, $\mathrm{C}\mathit{H}_{(1)}\mathrm{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2CH_2CH_3}$); $^2J_{\mathrm{H}_{(1)}\mathrm{H}_{(2)}} = 7.4$ Hz, $^3J_{\mathrm{H}_{(1)}\mathrm{H}_{(3)}} \approx 1$–2 Hz, $^3J_{\mathrm{H}_{(2)}\mathrm{H}_{(3)}} = 11.1$ Hz, $^2J_{103,\mathrm{RhH}_{(1)}} \cong {}^2J_{103,\mathrm{RhH}_{(2)}} \cong 2.5$ Hz, $^3J_{103,\mathrm{RhH}_{(3)}} \approx 0$ Hz. $^1$H NMR ($C_6D_6$) of isomer B: $\delta$ 8.44 (d, 8 H, pyrrole, $^3J_{\mathrm{HH}} = 4.6$ Hz), 8.42 (d, 8 H, pyrrole, $^3J_{\mathrm{HH}} = 4.6$ Hz), 7.23 (s, 8 H, mesityl meta $\mathrm{H}_{(\mathrm{out})}$), 6.97 (s, 8 H, mesityl meta $\mathrm{H}_{(\mathrm{in})}$), 2.40 (s, 24 H, mesityl para $CH_3$), 2.06 (s, 24 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{out})}$), 1.36 (s, 24 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{in})}$), 0.16 (t, 6 H, $\mathrm{CO_2CH_2C}\mathit{H}_3$), −4.82 (br s, 2 H, $\mathrm{CH}_{(1)}\mathrm{H}_{(2)}\mathrm{C}\mathit{H}_{(3)}\mathrm{CO_2CH_2CH_3}$), −4.82 (br s, 2 H, $\mathrm{CH}_{(1)}\mathit{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2CH_2CH_3}$), −5.80 (br, 2 H, $\mathrm{C}\mathit{H}_{(1)}\mathrm{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2CH_2CH_3}$).

The resonances for the $\mathrm{CO_2C}\mathit{H}_2\mathrm{CH_3}$ hydrogens are obscured by other peaks for both A and B complexes. Four of the high-field bridge hydrogen resonances of the B isomer have equivalent chemical shifts at room temperature. Taking the $^1$H NMR spectrum at 233 K in deuterated toluene resulted in the appearance of two broad multiplets evolving from the −4.82 ppm peak. FAB MS: *m/e* 1966.

**Reactions of (TMP)Rh$^\bullet$ with $CH_2{=}CH(CO_2H)$.** Mixing a $C_6D_6$ solution of (TMP)Rh$^\bullet$ with acrylic acid results in the immediate formation of (TMP)$RhCH_2CH(CO_2H)Rh$(TMP) followed by a slower reaction to produce an equilibrium distribution with a four-carbon-bridged complex, (TMP)$RhCH_2CH(CO_2H)CH(CO_2H)CH_2Rh$(TMP). Acrylate to (TMP)Rh$^\bullet$ mole ratios less than 10 produce (TMP)$RhCH_2CH(CO_2H)Rh$(TMP) as the only $^1$H NMR observable species, and mole ratios greater than 500 result in observing only (TMP)$RhCH_2CH(CO_2H)CH(CO_2H)CH_2Rh$(TMP). Only one of the two possible diastereomers is observed and assigned as the enantiomeric pair by $^1$H NMR.

**(TMP)$RhCH_2CH(CO_2H)Rh$(TMP).** $^1$H NMR ($C_6D_6$): $\delta$ 8.294 (d, 4 H, pyrrole $^3J_{\mathrm{HH}} = 4.6$ Hz), 8.276 (overlapping d, 2 × 4 H, pyrrole, $^3J_{\mathrm{HH}} = 4.6$ Hz), 8.257 (d, 4 H, pyrrole, $^3J_{\mathrm{HH}} = 4.6$ Hz), 7.26 (s, 4 H, mesityl meta $\mathrm{H}_{(\mathrm{out})}$), 7.24 (s, 4 H, mesityl meta $\mathrm{H}_{(\mathrm{out})}$), 6.88 (s, 4 H, mesityl meta $\mathrm{H}_{(\mathrm{in})}$), 6.86 (s, 4 H, mesityl meta $\mathrm{H}_{(\mathrm{in})}$), 2.41 (s, 12 H, mesityl para $CH_3$), 2.40 (s, 12 H, mesityl para $CH_3$), 2.25 (s, 12 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{out})}$), 2.23 (s, 12 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{out})}$), 0.95 (s, 12 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{in})}$), 0.90 (s, 12 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{in})}$), −6.19 (m, 1 H, $\mathrm{CH}_{(1)}\mathrm{H}_{(2)}\mathrm{C}\mathit{H}_{(3)}\mathrm{CO_2H}$), −6.79 (m, 1 H, $\mathrm{CH}_{(1)}\mathit{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2H}$), −7.32 (m, 1 H, $\mathrm{C}\mathit{H}_{(1)}\mathrm{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2H}$); $^2J_{\mathrm{H}_{(1)}\mathrm{H}_{(2)}} = 4.0$ Hz, $^3J_{\mathrm{H}_{(1)}\mathrm{H}_{(3)}} = 4.0$ Hz, $^3J_{\mathrm{H}_{(2)}\mathrm{H}_{(3)}} = 12.5$ Hz, $^2J_{103,\mathrm{RhH}_{(1)}} \cong {}^2J_{103,\mathrm{RhH}_{(2)}} \cong {}^2J_{103,\mathrm{RhH}_{(3)}} \cong 3$ Hz. The resonance for the hydrogen of the acid group was not found. FAB MS: *m/e* 1838.

**(TMP)$RhCH_2CH(CO_2H)CH(CO_2H)CH_2Rh$(TMP).** $^1$H NMR ($C_6D_6$): $\delta$ 8.42 (d, 8 H, pyrrole, $^3J_{\mathrm{HH}} = 4.7$ Hz), 8.39 (d, 8 H, pyrrole, $^3J_{\mathrm{HH}} = 4.7$ Hz), 7.21 (s, 8 H, mesityl meta $\mathrm{H}_{(\mathrm{out})}$), 6.98 (s, 8 H, mesityl meta $\mathrm{H}_{(\mathrm{in})}$), 2.39 (s, 24 H, mesityl para $CH_3$), 1.92 (s, 24 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{out})}$), 1.44 (s, 24 H, mesityl ortho $\mathrm{CH}_{3(\mathrm{in})}$), −4.96 (m, 2 H, $\mathrm{CH}_{(1)}\mathrm{H}_{(2)}\mathrm{C}\mathit{H}_{(3)}\mathrm{CO_2H}$), −5.76 (m, 2 H, $\mathrm{CH}_{(1)}\mathit{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2H}$), −6.46 (m, 2 H, $\mathrm{C}\mathit{H}_{(1)}\mathrm{H}_{(2)}\mathrm{CH}_{(3)}\mathrm{CO_2H}$); $^2J_{\mathrm{H}_{(1)}\mathrm{H}_{(2)}} = 7.3$ Hz, $^3J_{\mathrm{H}_{(1)}\mathrm{H}_{(3)}} \approx 1$–2 Hz, $^3J_{\mathrm{H}_{(2)}\mathrm{H}_{(3)}} = 9.7$ Hz, $^2J_{103,\mathrm{RhH}_{(1)}} \cong {}^2J_{103,\mathrm{RhH}_{(2)}} \cong 3.0$ Hz, $^3J_{103,\mathrm{RhH}_{(3)}} \approx 0$ Hz. The resonance for the acid hydrogens was not found. FAB MS: *m/e* 1910.

**Reaction of (TMP)Rh$^\bullet$ with Methyl Methacrylate.** The reaction reached completion by the time the $^1$H NMR spectrum was recorded. The two products forming in equal quantities were identified as (TMP)RhH and (TMP)$RhCH_2C(CO_2CH_3){=}CH_2$.

**(TMP)$RhCH_2C(CO_2CH_3){=}CH_2$.** $^1$H NMR ($C_6D_6$): $\delta$ 8.73 (s, 8 H, pyrrole), 4.26 (br s, 1 H, $-\mathrm{C}({=}\mathrm{C}\mathit{H}\mathrm{H})(\mathrm{CO_2CH_3})$), 2.56 (s, 3 H, $-\mathrm{CO_2C}\mathit{H}_3$), 2.45 (s, 12 H, mesityl para $CH_3$), 2.25 (s, 12 H, mesityl ortho $CH_3$), 1.87 (s, 12 H, mesityl ortho $CH_3$), −3.2 (br d, 2 H, $\mathrm{RhC}\mathit{H}_2-$, $^2J_{103,\mathrm{RhH}} = 3.5$ Hz). One of the $-\mathrm{C(CO_2CH_3){=}C}\mathit{H}_2$ hydrogen resonances is obscured by other peaks. FAB MS: *m/e* 982. (TMP)RhH was identified by the RhH resonance at $\delta$ −40.0 (d, $^1J_{\mathrm{RhH}} = 43.6$ Hz).

**Photoinduced (TMP)Rh$^\bullet$-Catalyzed Polymerization of Acrylates.** Polymerization reactions of acrylates used acrylate to (TMP)Rh$^\bullet$ ratios of 100–10000 which necessitates removal of the hydroquinone monomethyl ether inhibitor present at levels of 20–200 ppm in the acrylates. Results from polymerization studies were unchanged by using acrylate samples purified by chromatography on basic alumina or simply by vaccum transfer of the more volatile acrylate.

In a representative experiment, deuterated benzene (~0.3 mL) and an acrylate (~0.2 mL) were added to ~0.5 mg of (TMP)Rh$^\bullet$ through vacuum transfer and the sample was sealed. $^1$H NMR revealed the formation of the four-carbon-bridged dimer which reached completion by the time the $^1$H NMR spectrum was recorded at this high acrylate concentration. No further reaction was observed in the absence of light even at elevated temperatures (60–80 °C). Samples exposed to visible light started polymerizing immediately. Polymerization stopped when light was excluded and restarted again when samples were reexposed to light. Samples placed on the bench top exposed to regular fluorescent hoodlight from a distance of ~4 ft reached 80–90% conversion in 2–3 days. Using a projector lamp as a high-intensity light source (300-W tungsten bulb) from a distance of ~2 ft increased the rate of polymerization so that 90% conversion was reached in a period of 1–3 h. Experiments with a series of broad-range color filters revealed that polymerization is promoted by light with wavelengths below ~550 nm.

**$^1$H NMR Studies of the Polymer Systems.** The $^1$H NMR spectra of the polymers show four broad peaks centered at 2.6, 2.1, 1.8, and 1.55 ppm in a 2/1/2/1 ratio which correspond to a head to tail structure and a fully atactic arrangement of the $CO_2X$ units on the polymer chains. The ring current effect of the prophyrin units at the end of the polymer chains is manifested in an upfield shift of the closest polymer chain hydrogen resonances. These broad unstructured peaks appear in the −3.0 to −4.6 ppm and also in the −0.3 to −1.0 ppm regions (Figure 7). Proton decoupling experiments did not prove useful in assigning sets of high-field peaks.

**Molecular Weight Determination.** The polymerization process for the (TMP)Rh–methyl acrylate system was studied using gel permeation chromatography (GPC) to determine the number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$), and polydispersity ($M_w/M_n$) of poly(methyl acrylate) samples taken at increasing levels of conversion. Two procedures were used in performing the polymerization experiments.

**Method A.** A stock solution of (TMP)$RhCH_3$ (~1 mg/mL) in benzene was prepared, and equivalent 1-mL aliquots were placed in five vacuum-adapted NMR tubes. Each NMR tube was degassed by multiple freeze–pump–thaw cycles and subsequently photolyzed to produce (TMP)Rh$^\bullet$. The benzene solutions were evacuated to dryness, and sequentially deuterated benzene (~0.6 mL) and methyl acrylate (~0.4 mL) were vacuum transferred into the (TMP)Rh$^\bullet$ samples. The samples were sealed and exposed to visible light, and the polymerization process was monitored by $^1$H NMR. Polymerization was stopped at different conversions (5–80%) for each sample. The excess methyl acrylate and the benzene solvent were removed by evacuation. The polymer residue were redissolved in THF and analyzed by GPC.

**Method B.** Weighed samples of (TMP)$RhCH_3$ (~5 mg) were placed in vacuum-adapted tubes and dissolved in ~3 mL of dry

**Table II. Change in Molecular Weight Distribution with Changing Conversion in a Typical Photopromoted (TMP)Rh-Catalyzed Polymerization Experiment**[a]

| conversion | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|
| 6% | $1.75 \times 10^5$ | $3.06 \times 10^5$ | 1.75 |
| 17% | $2.18 \times 10^5$ | $3.93 \times 10^5$ | 1.80 |
| 37% | $2.68 \times 10^5$ | $5.41 \times 10^5$ | 2.02 |
| 78% | $1.44 \times 10^5$ | $3.98 \times 10^5$ | 2.76 |

[a] Number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$), and polydispersity ($M_w/M_n$) values of poly(methyl acrylate) samples taken at different conversion levels.

benzene which was transferred via the vacuum line. After photolysis the sample was evacuated to dryness and subsequently redissolved in dry, degassed $C_6D_6$ (~3 mL). Inside an inert atmosphere box the solution was syringed into a volumetric flask together with an additional 3 mL dry degassed $C_6D_6$ and 4 mL of methyl acrylate. Methyl acrylate was chromatographed on grade I basic alumina to remove inhibitor and degassed prior to addition. The mixture was exposed to visible light, and 1–2-mL samples were removed during the polymerization process by use of a syringe. The conversion for each sample was determined by $^1$H NMR, and subsequently the solutions were evacuated to remove excess methyl acrylate and benzene solvent. The polymer residue was redissolved in THF for GPC measurement. Results from using methods A and B were in substantial agreement.

**GPC Results.** A refractive index (RI) detector was used in determining the number-average molecular weight ($M_n$), the weight-average molecular weight ($M_w$), and polydispersity ($M_w/M_n$) of each sample. The instrument was calibrated using monodispersed polystyrene standards. UV–vis detection ($\lambda$ = 420 nm) was used to determine the presence of the (TMP)Rh units in the polymer.

In a typical polymerization experiment, 4–5 samples were analyzed with conversions varying from 5% to 80%. At conversions up to 40–50%, polydispersity was in the 1.4–2.0 range and $M_w$ and $M_n$ values increased with increasing conversion. At conversions greater than 50%, the polydispersity became significantly larger ($2 < M_w/M_n < 4$) with a parallel decrease in both $M_w$ and $M_n$ values of the samples (Table II). UV–vis detection at 420 nm indicated that a large portion of the (TMP)Rh units present in the system were attached to polymer chains but that some low molecular weight fragments containing (TMP)Rh occur at all stages of the polymerization.

**Acknowledgment.** We gratefully acknowledge support of this work by the National Science Foundation and by E.I. du Pont de Nemours and Co.

OM920196E

---

# New Silane-Induced CO Activation in $[(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_2\cdot THF]$: Formation of the Cyclic Bis($\mu$-carbyne) Complex $(\eta^5\text{-}H_3CC_5H_4)(CO)Mn(\mu\text{-}COSiH(t\text{-}Bu)_2)_2Mn(CO)(\eta^5\text{-}H_3CC_5H_4)$ and the CC-Coupling Reaction of the Siloxy–Carbyne Ligands

Hermann Handwerker, Holger Beruda, Matthias Kleine, and Christian Zybill*

*Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, W-8046 Garching, Federal Republic of Germany*

*Received April 30, 1992*

The labile complex $[(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_2\cdot THF]$ (6) is generated by photolysis of $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_3$ (5) and subjected to oxidative addition reactions with various silanes. With $(t\text{-}Bu)_2SiHCl$ (7) the cyclic bis($\mu$-carbyne) complex $(\eta^5\text{-}H_3CC_5H_4)(CO)Mn(\mu\text{-}COSiH(t\text{-}Bu)_2)_2Mn(CO)(\eta^5\text{-}H_3CC_5H_4)$ (8) is formed in 15% yield. A systematic investigation of the product distribution in these reactions shows that the formation of bis($\mu$-carbyne) complexes versus silylmetal hydrides is a strong function of the substituents at the silane. Reaction of $[(\eta^5\text{-}EtMe_4C_5)Mn(CO)_2\cdot THF]$ (19) with 7 also gives, besides formation of the bis($\mu$-carbyne) complex $[(\eta^5\text{-}EtMe_4C_5)(CO)Mn(\mu\text{-}COSiH(t\text{-}Bu)_2)_2Mn(CO)(\eta^5\text{-}EtMe_4C_5)]$ (20), the triply bridged carbonyl complex $(\eta^5\text{-}EtMe_4C_5)Mn(\mu\text{-}CO)_3Mn(\eta^5\text{-}EtMe_4C_5)$ (22). A single-crystal X-ray structure determination of 8 shows a cyclic four-membered ring structure with a bond distance Mn–C15 (carbyne C) of 1.857 (2) Å. The metallacycle is folded along the Mn–Mn bond (2.565 (1) Å) which is in accordance with an all-trans geometry of the ring substituents. This ring geometry opens up a reaction pathway for 1,3-cis elimination reaction of bis(siloxy)ethyne $[(t\text{-}Bu)_2HSiOC{\equiv}]_2$ (9) via a CC-coupling reaction of both carbyne units as well as the elimination of disilyl peroxide $[(t\text{-}Bu)_2HSiO\text{-}]_2$ (10). Compound 8 crystal data: monoclinic, $C2/c$, $a$ = 31.283 (3) Å, $b$ = 8.350 (1) Å, $c$ = 16.312 (2) Å, $\beta$ = 126.63 (1)°, $Z$ = 8.

## Introduction

The reductive coupling of metal-coordinated carbon monoxide is a current research objective, particularly with regard to the goal of CO conversion reactions (Fischer–Tropsch synthesis).[1] Key steps in the metal-mediated CO-coupling reaction are CO activation and reduction and subsequent CC coupling of the highly reactive carbyne units in the coordination sphere of a transition metal. Lippard has recently shown that the siloxycarbyne complex $[Ta({\equiv}COSiR_3)(CO)(dmpe)_2]$ (2) is a stable intermediate in the reduction of $[Ta(CO)_2(dmpe)_2Cl]$ (1) with Na/Hg in the presence of $R_3SiCl$ to the acetylene complex $[Ta(R_3SiOC{\equiv}COSiR_3)(dmpe)_2Cl]$ (3).[2,3] A CO-bridged dinuclear tantalum siloxycarbyne complex 4 was also isolated from this reaction[4] (eq 1). Similar results have been

---

(1) Vrtis, R. N.; Lippard, S. J. *Isr. J. Chem.* **1990**, *30*, 331.

(2) Vrtis, R. N.; Bott, S. G.; Rardin, L.; Lippard, S. J. *Organometallics* **1991**, *10*, 1364–1373.

(3) For $\eta^2$-ketenyl intermediates see ref 1.