C-H Bond Activation in Cp$_2$Zr^{III}CH$_2$PPh$_2$: Evidence for an Unexpected Mechanistic Pathway

Claudine Blandy,[1] Susan A. Locke, Steven J. Young, and Neil E. Schore*

Department of Chemistry, University of California Davis, California 95616

Received June 27, 1988

In the course of our earlier studies of the chemistry of Cp$_2$Zr(Cl)CH$_2$PPh$_2$ (**1**) we found that reduction of alkyl-zirconocene chlorides [Cp$_2$Zr(Cl)R, R = e.g., *n*-octyl] by Na/Hg in tetrahydrofuran (THF) gave rise to high yields of the corresponding alkane, RH. In addition, a Zr-containing species was formed which was trapped in equally high yield by phosphines, e.g., MePPh$_2$, in the form of [CpZr(PMePh$_2$)]$_2$[μ-(η^1:η^5-C$_5$H$_4$)]$_2$ (**2**). Double-labeling experiments revealed the process to be intermolecular with H transferred from a Cp ring to the alkyl group R, and evidence was obtained for the initial intermediacy of Cp$_2$Zr^{III}R. On the basis of evidence against radical intermediates, we suggested an even-electron, "four-center" mechanism.[2] We also found that the reduction of **1** itself allowed isolation of paramagnetic Cp$_2$Zr^{III}(η^2-CH$_2$PPh$_2$) (**3**) and ultimately also gave rise to **2**, lending support to this mechanism and suggesting that **1** was special only in that the Zr^{III} intermediate was unusually stabilized when R = CH$_2$PPh$_2$. We noted, however, that both reduced solutions of **1** and "purified" preparations of **3** invariably exhibited an enigmatic, characteristically broad 90 MHz proton NMR resonance at δ 5.5 in THF.[3] We report herein the characterization of the compound responsible for this resonance, a preliminary examination of its chemistry, and implications of these results regarding pathways for C-H bond activation at higher valent transition-metal centers.

Examination of the proton NMR spectra at 360 and 500 MHz of apparently pure **3** in C$_6$D$_6$ reveals that the broadened feature resolves into two singlets which form just a portion of a very complex spectrum. Although the compound responsible for these signals is only a minor component (perhaps 20%) of a mixture predominantly containing paramagnetic **3**, all NMR signals are sharp and well-resolved. No NMR signals for **3** are observed. The proton spectrum[4] contains signals for three Cp rings, the four individual protons of a C$_5$H$_4$ unit, four protons of two diastereotopic methylenes, and a single proton at δ 3.02 split into a doublet with J = 76 Hz. In order to obtain complete ^{31}P and ^{13}C NMR data we prepared and reduced Cp$_2$Zr(Cl)^{13}CH$_2$PPh$_2$ (^{13}1).[5] The ^{31}P and ^{13}C NMR spectra for the diamagnetic product show signals for one ^{13}CH$_2$PPh$_2$ group at δ (^{31}P) -2.7 and δ (^{13}C) 44.5 coupled with J_{CP} = 45 Hz [compare ^{13}1 which shows δ (^{31}P) -1.2, δ (^{13}C) 47.5, and J_{CP} = 44 Hz]. Signals for a second ^{13}CH$_2$PPh$_2$ group appear at δ (^{31}P) 45.2 and δ (^{13}C) 43.1 with J_{CP} = 12 Hz. In the absence of proton decoupling, the latter signals also show J_{PH} = 76 Hz and a long-range J_{CH} = 3.5 Hz (present in the δ 3.02 proton signal as well), strongly suggesting that this group is linked to a Zr-H moiety. These data uniquely define the structure of the diamagnetic material to be the dinuclear hydride **4**, a totally unprecedented species in Zr chemistry.[6]

4
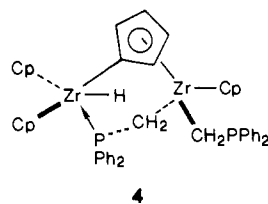
Further characterization of **4** has been obtained from its chemical behavior. Reaction with CH$_3$I confirms the presence of the metal hydride, forming 1 equiv of methane. Reaction of **4** with PMe$_3$ forms several products including significant amounts of Cp$_2$Zr(CH$_2$PPh$_2$)$_2$ and Cp$_2$Zr(PMe$_3$)$_2$, presumably via reductive elimination of Zr^{II} from the Cp C-H bond followed by complexation by the less sterically demanding phosphine.[7]

The formation of **4** can be rationalized as follows. Reduction of **1** initially gives a species Cp$_2$Zr^{III}CH$_2$PPh$_2$ in which Zr-P bonding is lacking. In a weakly coordinating solvent (e.g., C$_6$D$_6$) ring closure occurs essentially exclusively to form **3**; little **4** is observed.[8] However, upon reduction of **1** in THF, ring closure may be partially inhibited by solvent complexation,[9] allowing instead a bimolecular *disproportionation* to occur via Zr-to-Zr transfer of an alkyl (i.e., phosphinomethyl) moiety. The result is a dinuclear intermediate containing a Zr^{II} center, ideally situated to activate a Cp C-H bond *by conventional oxidative addition* (eq 1).[10] Thus the need for invoking a concerted four-center

(1)
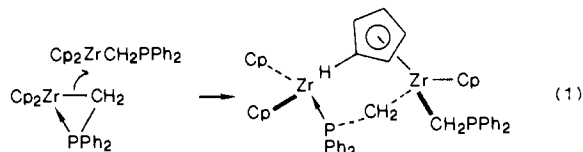
activation mechanism is removed. To our knowledge this particular type of pathway, involving spontaneous disproportionation of a metal in its next-to-highest oxidation state to lead to a metal center capable of C-H activation by oxidative addition (i.e., 2d^1 $\rightarrow$ d^0 + d^2), is unprecedented.[11] The intermediacy of **4** also explains the formation of substantial amounts of Cp$_2$Zr-(CH$_2$PPh$_2$)$_2$ in reductions of **1**. It should be noted that disproportionation of **1** does not occur in the absence of reducing conditions: Cp$_2$ZrCl$_2$, Cp$_2$Zr(CH$_2$PPh$_2$)$_2$, and **1** are completely stable individually as well as in each others presence in all solvents that we have examined.[12]

(6) Compare NMR of (η^5-C$_5$Me$_5$)$_2$Zr(H)$_2$(PF$_3$), in which J_{HZrP} = 108 Hz: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733. These data do not distinguish between possible stereoisomers at the Zr-H center. All splittings have been confirmed either in the spectra of all involved nuclei or via 2-D NMR techniques.

(7) The PMe$_3$ analogue of **2** and several unidentified Cp-containing species are formed. Spectrum is available in the Supplementary Material.

(8) Interestingly, upon reduction of Cp$_2$Zr(Cl)CH$_2$P*Me$_2$*, only Cp$_2$Zr^{III}-(η^2-CH$_2$PMe$_2$) is formed irrespective of solvent, presumably a result of the greater ease of intramolecular complexation by the smaller phosphine.

(9) Cf. Lappert, M. F.; Ralston, C. L. *J. Chem. Soc., Chem. Commun.* **1981**, 173.

(10) Precedented in the first studies concerning compound **2**: Gell, K. I.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 481. See, also: Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1985**, 224.

(11) C-H activation and related processes occurring at d^0 metal centers involve either a four-center mechanism or, rarely, electrophilic aromatic substitution. The same has typically been assumed to be the case for d^1 centers as well. Reviews: (a) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153. (b) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (c) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139. See, also: (d) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939. (e) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650. (f) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (g) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (h) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (i) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (j) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1.

(12) Not surprisingly, treatment of a mixture of Cp$_2$ZrCl$_2$ and Cp$_2$Zr-(CH$_2$PPh$_2$)$_2$ with Na/Hg does lead to transient formation of some **1**, although most of the Cp$_2$Zr(CH$_2$PPh$_2$)$_2$ remains unreacted as the Cp$_2$ZrCl$_2$ is consumed. Reduction of Cp$_2$ZrCl$_2$ with Na/Hg is known to be a poor method for generation of reactive "Cp$_2$Zr" fragments: Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

(1) On leave from Laboratoire de Chimie de Coordination du CNRS, Université Paul Sabatier, 31077 Toulouse Cedex, France.

(2) (a) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251. (b) Schore, N. E.; Young, S. J.; Olmstead, M. M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769.

(3) See center NMR trace in Figure 5 of ref 2b.

(4) Complete proton NMR: (C$_6$D$_6$, 360 and 500 MHz) δ -0.28 (t, J = 12 Hz, 1 H), 0.87 (dd, J = 4, 10 Hz, 1 H), 1.13 (dd, J = 4, 10 Hz, 1 H), 1.38 (t, J = 12 Hz, 1 H), 3.02 (d, J = 76 Hz, 1 H), 5.08 (br s, 1 H), 5.39 (br s, 1 H), 5.41 (br s, 5 H), 5.46 (br s, 5 H), 5.83 (br s, 1 H), 5.89 (s, 5 H), 6.28 (br s, 1 H); phenyl absorptions partially obscured by C$_6$D$_5$H signal. Spectrum is available in the Supplementary Material.

(5) Via the sequence ^{13}CH$_3$I $\rightarrow$ ^{13}CH$_3$MgI $\rightarrow$ ^{13}CH$_3$PPh$_2$ $\rightarrow$ Li^{13}CH$_2$PPh$_2$ $\rightarrow$ Cp$_2$Zr(Cl)^{13}CH$_2$PPh$_2$. Upon reduction of ^{13}1 the ^{13}C analogue of **3** (^{13}3) is also formed, showing in the ESR an a(^{13}C) = 7.2 G in addition to the ^{31}P and ^{91}Zr splittings reported earlier.[2]

Communications to the Editor

J. Am. Chem. Soc., Vol. 110, No. 22, 1988 7541

The thermal chemistry of **4** has been explored by NMR (Figure 1). It is labile even at room temperature in solution, and heating of a C_6D_6 solution of **4** by partial immersion in a 55 °C bath indeed leads to substantial amounts of **2**. One can speculate that this conversion involves elimination of $MePPh_2$, generating a $Zr^{III}-Zr^{III}$ system in which disproportionation followed by C–H activation involving a second Cp ring may again occur as above. Elimination of a second $MePPh_2$ followed by complexation by the phosphines would lead directly to **2** (eq 2).
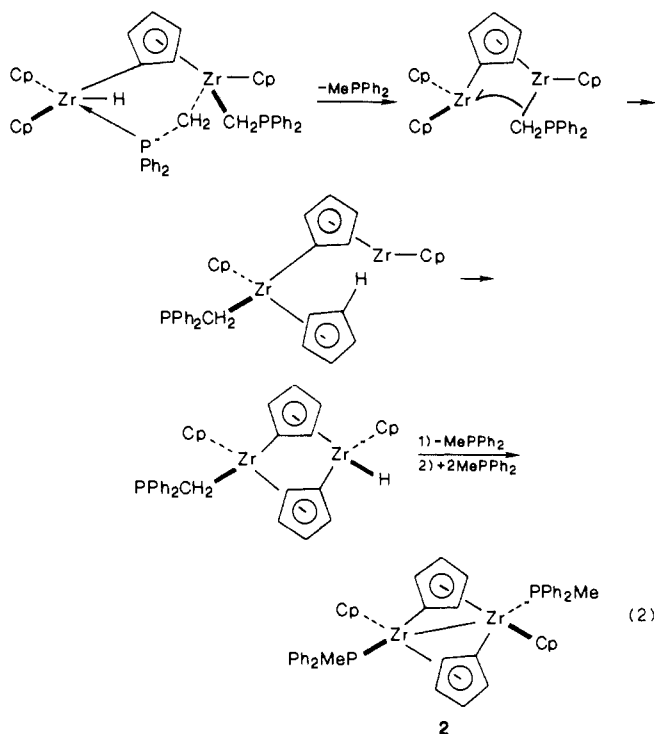
Free $MePPh_2$ is formed upon thermolysis of **4** together with a second organometallic product which remains only partially characterized due to its own thermal lability. It is still a metal hydride and possesses a $CHPPh_2$ unit.[13] The released $MePPh_2$ is thus formally derived from one of the CH_2PPh_2 groups and a hydrogen from the *methylene* of the other. Continued thermolysis gives a compound with a new low-field (bridging?) CH_2 no longer bonded to phosphorus.[14] Efforts aimed at isolation and complete characterization of these materials are continuing.[15]

Nonetheless, it is now clear that the C–H activation mechanism in $Cp_2Zr^{III}CH_2PPh_2$ need not directly involve d^1 Zr^{III} at all and instead may proceed after facile disproportionation via oxidative addition to a d^2 Zr^{II} center. It seems reasonable to extend these conclusions to $Cp_2Zr^{III}R$ in general, although direct evidence is lacking at this time. The chemistry of U^{III}, while quite different in detail, possesses some similarities in its ease of disproportionation as well as high reactivity toward hydrogenolysis of σ-bound alkyl groups compared with U^{IV},[16] although no connection between the two forms of behavior was established. Whether such a sequence can be generalized to other d^1 metals is a question we hope to answer in the near future.

(13) Partial NMR data (^{13}C-labeled series): ^{1}H δ 1.70 (J_{PH} = 47 Hz), 4.28 (J_{PH} = 6 Hz, J_{CH} = 122 Hz); ^{13}C δ 83.2 (J_{CP} = 49 Hz); ^{31}P δ 41.2 (see species X, middle trace, Figure 1).

(14) CMR: δ (^{13}C) 161.8; cf. δ (^{13}C) 173.1 in $Cp_2Zr(\mu$-$CH_2)_2ZrCp_2$: van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1986**, *308*, 1.

(15) With one exception, the presence of paramagnetic **3** does not complicate these experiments as diamagnetic products are in fact *not* formed from it in appreciable amounts under the conditions described. Reaction with MeI is more complex and will be described in detail elsewhere.

(16) (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170. (b) Finke, R. G.; Hirose, Y.; Gaughan, G. *J. Chem. Soc., Chem. Commun.* **1981**, 232. (c) Finke, R. G.; Schiraldi, D. A.; Hirose, Y. *J. Am. Chem. Soc.* **1981**, *103*, 1875.
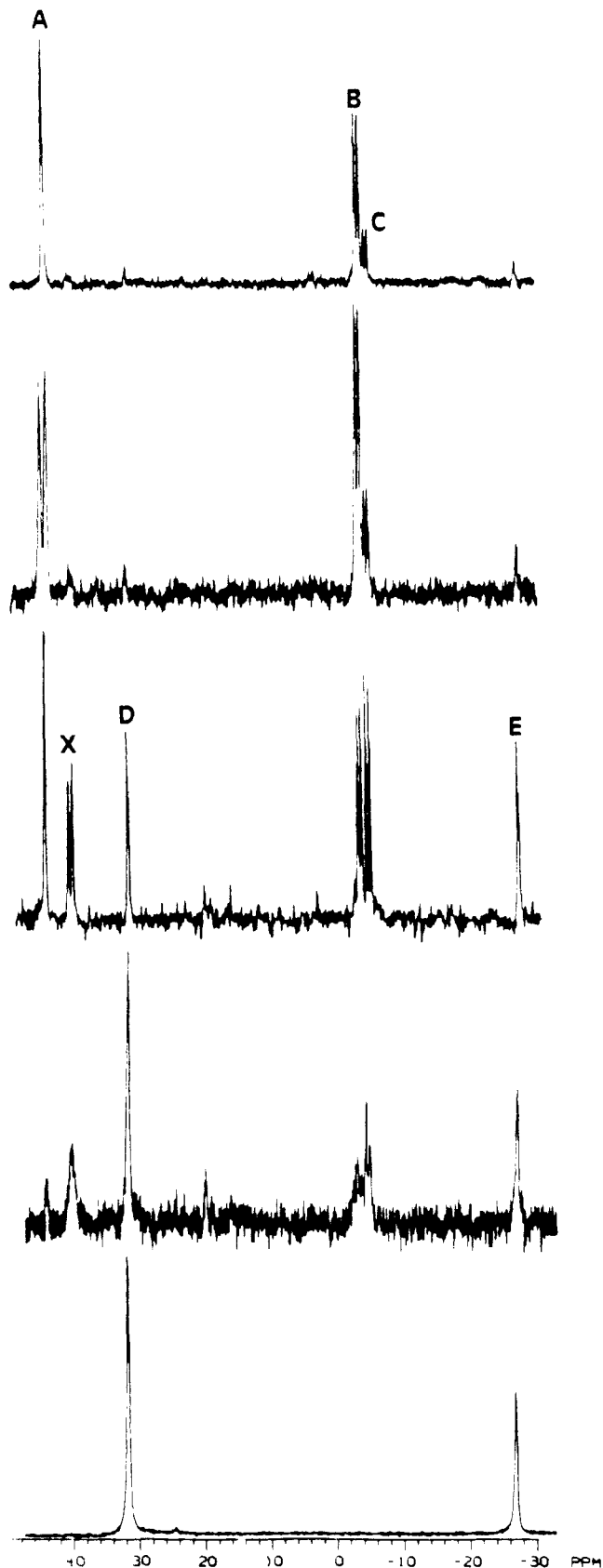
Figure 1. ^{31}P{^{1}H} NMR spectra depicting thermolysis of ^{13}**4**. First trace: C_6D_6 solution of ^{13}**4** (signals A and B), containing a small amount of $Cp_2Zr(^{13}CH_2PPh_2)_2$ (C). Second trace: same, without {^{1}H}, showing J_{PH} = 76 Hz for signal A. Third trace: after 2 h at 55 °C, showing formation of ^{13}**2** (D), $^{13}CH_3PPh_2$ (E), additional $Cp_2Zr(^{13}CH_2PPh_2)_2$, and transient species (X, see text and ref 13). Fourth trace: after 6 h at 55 °C (vertical scale different). Fifth trace: C_6D_6 solution of $^{13}CH_3PPh_2$ and authentic ^{13}**2** [prepared from reduction of $Cp_2Zr(n$-$C_8H_{17})Cl$ in the presence of $^{13}CH_3PPh_2^{2b,10}$].

Supplementary Material Available: Proton NMR spectrum for 4 and spectrum illustrating result of reaction of 4 with PMe₃ (2 pages). Ordering information is given on any current masthead page.

Catalytic Organometallic Chemistry in Water: The Aqueous Ring-Opening Metathesis Polymerization of 7-Oxanorbornene Derivatives[†]

Bruce M. Novak and Robert H. Grubbs*

*Arnold and Mabel Beckman Laboratory of Chemical
Synthesis, California Institute of Technology
Pasadena, California 91125*

Received June 28, 1988

The sensitivity of organometallic catalysts[1] to oxygen, water, and heteroatom functionalized substrates has often hampered their evolution from research laboratories to full-scale, on-line industrial processes.[2] In our efforts to develop ring-opening metathesis polymerization (ROMP)[3] catalysts which are compatible with functionalized monomers, we have found that select group VIII coordination complexes[4] will rapidly polymerize derivatives of 7-oxanorbornene *in aqueous solution under an atmosphere of air* to provide quantitative yields of the desired ROMP polymer.[5] The synthetic utility of these aqueous emulsion systems is considerably expanded with the finding that metal–olefin coordination complexes formed in situ during the polymerization of the 7-oxanorbornene monomers are highly active toward both subsequent polymerizations and the polymerization of other monomers hitherto unreactive in aqueous solution. This extraordinary stability to air and water displayed by normally highly reactive organometallic intermediates (metal carbenes and metallacyclobutanes) suggests the intriguing possibility that classical coordination complexes might find a wider application in other, established (but sensitive) catalytic processes.

We recently reported the ROMP of 7-oxanorbornene derivatives in dry organic solvents by using a variety of transition-metal catalysts.[6] The most successful[7] catalysts were systems based

on the group VIII metal complexes such as RuCl₃(hydrate)[8] and OsCl₃(hydrate)(eq 1).

$$R = H.\ I$$
$$R = CH_3.\ II$$
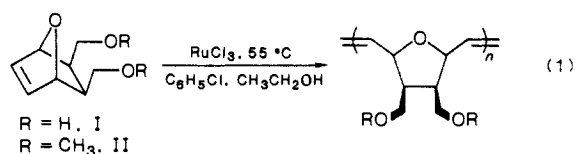
Polymerizations using these group VIII metals are preceded by a sometimes lengthy initiation period that effectively limits their usefulness.[9] It is during this initiation period that a small amount of reactive metal carbene is formed,[10] which then very rapidly polymerizes the cyclic olefin present.[11] During our efforts to decrease this initiation period (typically 22–24 h for II in organic solvents) we found that rigorous exclusion of water from the reaction mixture actually had an unexpected effect.[12] Rather than deactivating these metal catalysts, water actually acts as a cocatalyst by dramatically decreasing the initiation period required for the reaction. This unusual finding eventually culminated in the discovery that the polymerization of the 7-oxanorbornene derivatives proceeds rapidly *in water alone* to produce the desired ROMP polymer in nearly quantitative yields. Initiation times decreased from the 22–24 h by using organic solvents to 30–35 min in aqueous solution.[13]

Another key consideration in metal-mediated catalytic systems is the recyclability of the catalyst. In examining the used aqueous ruthenium solutions after an initial polymerization of II, it was found that not only is the solution recyclable but that these used catalysts actually become more active in subsequent polymerizations. The initiation period drops from the initial value of 37.5 min for the polymerization of II to a limiting value (after two to three polymerizations) of only 10–12 s.[14] Solutions containing these aqueous catalysts have been recycled for up to 14 successive polymerizations without any detectable loss of activity. Overall, this represents an approximate 5000-fold increase in the initiation rate upon changing from the organic solvent systems to these recycled aqueous catalyst systems.

The aqueous polymerization of II by the very active Ru-(H₂O)₆(tos)₂ (tos = *p*-toluenesulfonate)[15] salt shows the same basic trends as did the Ru³⁺ complexes, i.e., increasing activity with use.[16] When *n* equiv of II are allowed to react with Ru-

[†] Contribution No. 7806.

(1) Parshall, G. W. *Homogeneous Catalysis;* Wiley: New York, 1980.

(2) (a) Ziegler, K. *Angew. Chem.* **1955,** *65,* 426. (b) Kuntz, E. G. *CHEMTECH* **1987,** *570.* (c) Chung, T. C. *Macromolecules* **1988,** *21,* 865.

(3) For recent references on metathesis, see: (a) Ivin, K. J. *Olefin Metathesis;* Academic Press: London, 1983. (b) Grubbs, R. H. In *Comprehensive Organometallic Chemistry;* Wilkinson, G., Ed.; Pergamon Press, Ltd.: Oxford, 1982; Vol. 8, pp 499–551.

(4) For examples of catalysis by group VIII complexes in organic solvents, see: (a) Ho, H. T.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1982,** *15,* 245. (b) Porri, L.; Diversi, P.; Lucherini, A.; Rossi, R. *Makromol. Chem.* **1975,** *176,* 3131. (c) Porri, L.; Rossi, R.; Diversi, P.; Lucherini, A. *Makromol. Chem.* **1974,** *175,* 3097.

(5) Early attempts at emulsion ROMP systems have been reported. These systems, however, either fail for many monomers or, at best, give low yields of polymer (typically less than 9%). See: Rhinehart, R. E.; Smith, H. P. *Polym. Lett.* **1965,** *3,* 1049.

(6) (a) Novak, B. M.; Grubbs, R. H. *Proc. Am. Chem. Soc. Div. PMSE* **1987,** *57,* 651. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988,** *110,* 960.

(7) "Successful" as used herein refers to high yields (>95%) of high molecular weight polymers (>1 × 10⁵).

(8) Commercial RuCl₃ (hydrate) is actually an ill-defined mixture of several oxo-chloro species of varying oxidation states. The same catalytic chemistry is observed, however, when well characterized Ru³⁺ is used. See: Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium;* Elsevier: New York, 1984; pp 159.

(9) This initiation period can be on the order of hours to days depending on the particular monomer and catalyst employed. For example, the RuCl₃ catalyzed aqueous polymerization of norbornene (with emulsifiers) is preceded by an initiation period of 8 days at 55 °C.

(10) (a) Ivin, K. J. *Olefin Metathesis;* Academic Press: London, 1983; pp 43–78. (b) Grubbs, R. H. In *Comprehensive Organometallic Chemistry;* Wilkinson, G., Ed.; Pergamon Press, Ltd.: Oxford, 1982; Vol. 8, pp 499–551.

(11) Once initiated, the polymerization proceeds at a very high rate. The initial rate of polymerization can be estimated from NMR studies and molecular weight data to be on the order of 750–1000 equiv/min. We have therefore concentrated on developing methods of increasing the initiation rates for these group VIII complexes.

(12) Standard Schlenk line techniques utilizing dry Ar were employed. Benzene was distilled from sodium benzophenone ketyl, monomer II was vacuum transferred from NaH, and ethanol was azeotrope-distilled with benzene.

(13) The benefits of aqueous emulsion polymerization techniques are well documented. For the polymerization of II the molecular weight increases by a factor of 4, from $M_w = 3.38 \times 10^5$ to 1.34×10^6, and the polydispersity (PDI) drops from 1.97 to 1.2 upon changing from organic to aqueous solvents. See: (a) Odian, G. *Principles of Polymerization,* 2d ed.; Wiley-Interscience: New York, 1981; p 319. (b) Hiemenz, P. C. *Polymer Chemistry;* Marcel Dekker, Inc.: New York, 1984; p 396.

(14) As far as we can determine, this increase in catalyst activity is unique to the ROMP of the 7-oxanorbornene monomers. For example, the catalyst solution resulting from a polymerization of norbornene is recyclable; however, no enhancement of the initiation rate is observed for subsequent polymerizations.

(15) (a) Bernhard, P.; Lehmann, H.; Ludi, A. *J. Chem. Soc., Chem. Commun.* **1981,** 1216. (b) Bernhard, P.; Burgi, H. B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982,** *21,* 3936.