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Supplementary Material Available: Proton NMR spectrum for **4** and spectrum illustrating result of reaction of **4** with PMe_3 (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[†]

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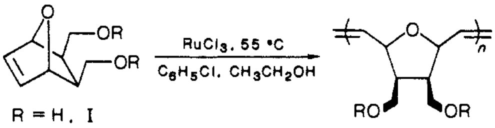
The sensitivity of organometallic catalysts[1] to oxygen, water, and heteroatom functionalized substrates has often hampered their evolution from research laboratories to full-scale, on-line industrial processes.[2] In our efforts to develop ring-opening metathesis polymerization (ROMP)[3] catalysts 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 $RuCl_3$(hydrate)[8] and $OsCl_3$(hydrate)(eq 1).



(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 $Ru(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate)[15] salt shows the same basic trends as did the Ru^{3+} complexes, i.e., increasing activity with use.[16] When *n* equiv of II are allowed to react with Ru-

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[†] 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 × 10^5).

[8] Commercial $RuCl_3$ (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 Ru^{3+} 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 $RuCl_3$ 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.

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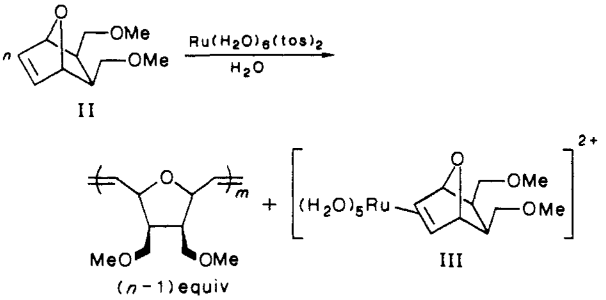
$(H_2O)_6(tos)_2$ in D_2O, (n − 1) equiv of II are polymerized, and conversion of the catalyst to the mono-olefin adduct $Ru(H_2O)_5(II)(tos)_2$, III, (λ_{max} = 294 nm) is observed by NMR (eq 2).[17]



(2)

Aqueous solutions of III are highly active in subsequent polymerizations, displaying the same rapid initiation times (10–12 s) as the limiting initiation times observed for the recycled Ru^{3+} solutions. We therefore attribute the increased activity of the recycled catalyst solutions to the in situ formation of Ru^{2+} olefin complexes.[18] When the polymerization of II is carried out by using Ru^{3+} salts ($RuCl_3$ or K_2RuCl_5) in D_2O to generate the active catalyst solution, resonances identical with the olefin resonances of adduct III are observed.[17] Because Ru^{3+} does not form stable olefin complexes,[19] we therefore conclude that these resonances are due to Ru^{2+} olefin adducts formed from the reduction of Ru^{3+} in the reaction mixture. On the basis of formation of Ru^{4+} (as Ru Red, λ_{max} = 544 nm)[20] and a Ru^{2+} olefin complex[21] when II is polymerized by $Ru(NH_3)_5(H_2O)^{3+}$ (λ_{max} = 325 nm), we propose a mechanism which involves the disproportionation of an equilibrium amount of Ru^{3+}–olefin complex to provide a Ru^{2+}–olefin complex and a Ru^{4+} species which is trapped by additional Ru^{3+}. The olefin complex thus produced initiates the observed polymerization chemistry.

The synthetic utility of these aqueous polymerization systems can be expanded to include monomers that are reluctant to polymerize in aqueous solution by using the preformed olefin complex III to catalyze the polymerization. For example, the K_2RuCl_5 catalyzed aqueous polymerization of 2-norbornene-5-methanol provides at best only low yields of the desired polymer (typically <10%). Under the similar conditions with III as the catalyst, yields greater than 90% are obtained.

Our current work on these aqueous ROMP systems is focusing on both the systematic modifications of these classical coordination complexes to enhance and understand their organometallic chemistry as well as the utilization of these new catalysts in the polymerization of highly functionalized monomers.

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(16) The Ru^{2+} is far more active, with an initiation time of 50–55 s for the first polymerization. The recycled catalyst displays subsequent initiation times of 10–12 s.

(17) Characteristic changes in the spectra of the complexed monomer relative to that of free monomer are upfield shifts of the olefinic proton (6.28 to 5.07 ppm) and carbon (135.2 to 84.6 ppm) signals and downfield shifts of the endo proton (1.77 to 2.54 ppm) and carbon (39.6 to 42.6 ppm) signals. Compound III: ^1H NMR (400 MHz, D_2O); olefinic moiety: 5.08 (s), 4.73 (s), 3.44 (m), 3.26 (s), and 2.54 (m) ppm. Tosylate anion: 7.52, 7.50, 7.19, 7.17, and 2.21 ppm. ^{13}C NMR (D_2O); olefinic moiety: 84.6, 77.2, 71.5, 58.9, and 44.6 ppm. Tosylate anion: 143.3, 140.2, 130.2, 126.1, and 21.25 ppm. The cyclic voltammogram of complex III shows one irreversible Ru^{2+}/Ru^{3+} oxidation couple at 1.05 V versus SSCE. This represents an overall stabilization of the Ru^{2+} state by 1.08 V. For a discussion of the stabilization of low valent Ru complexes by electron acceptor ligands, see: Sullivan, B. P.; Baumann, J. A.; Meyer, T. J.; Salmon, D. J.; Lehmann, H.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7368.

(18) In the cases where specific monomers form no olefin complexes in the reaction mixture, no enhancement of activity is observed upon repeated use of the catalyst solution. An example of this would be multiple polymerizations of norbornene (see footnote 14).

(19) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: New York, 1984.

(20) Ru^{4+} formed in the presence of Ru^{3+} and NH_3 reacts rapidly to form the mixed valent trimer "Ru Red". See: (a) Fletcher, J. M.; Greenfield, B. F.; Hardy, C. J.; Scargill, D.; Woodhead, J. L. *J. Chem. Soc.* **1961**, 2000. (b) Sterling, C. *Amer. J. Bot.* **1970**, *57*, 172. (c) Smith, P. M.; Fealey, T.; Earley, J. E.; Silverton, J. V. *Inorg. Chem.* **1971**, *10*, 1943.

(21) Several Ru^{2+} olefin complexes are known. See: (a) Sullivan, B. P.; Baumann, J. A.; Meyer, T. J.; Salmon, D. J.; Lehmann, H.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7368. (b) Lehmann, H.; Schenk, K. J.; Chapuis, G.; Ludi, A. *J. Am. Chem. Soc.* **1979**, *101*, 6197.

A New Structural Form of Tin as a Double Cube. A Heptanuclear Tin–Sulfur Cluster

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Recently, we reported new classes of organooxotin compounds in the form of cubes,[1,2] drums,[3-6] and oxygen-capped clusters.[2,6,7] The faces of these clusters consist of either four- or six-membered Sn–O rings. The cube and the drum have the same empirical composition, $[R'Sn(O)O_2PR_2]_n$, n = 4 and 6, respectively, whereas the oxygen-capped cluster, $[(R'Sn(OH)O_2PR_2)_3O][R_2PO_2]$, resembles a cube with one corner missing. ^{119}Sn NMR spectra show that the drum[6] and the cube[2] forms undergo hydrolysis in solution giving oxygen-capped clusters. Heating the latter regenerates the starting drum[6] or cube,[8] thus showing the reaction to be reversible. In all of these compositions, tin is hexacoordinated, and chelating phosphinate or phosphate ligands span adjacent tin atoms.

In our continuing exploration of new oligomeric formulations and their structural interconversions, we now report the first heptanuclear tin–sulfur cluster formed from the reaction of n-butylstannonic acid, diphenyl phosphine oxide, and elemental sulfur.[9]

$$24Ph_2P(OH) + 3S_8 + 28n\text{-}BuSn(O)OH \xrightarrow[\text{reflux}]{\text{toluene}} 4[\{n\text{-}BuSnS(O_2PPh_2)\}_3O]_2Sn + 24H_2O + 4n\text{-}BuH$$

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(1) Kumara Swamy, K. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 5546.

(2) Holmes, R. R.; Kumara Swamy, K. C.; Schmid, C. G.; Day, R. O. *J. Am. Chem. Soc.* **1988**, *110*, 7060.

(3) Chandrasekhar, V.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1985**, *24*, 1970.

(4) Holmes, R. R.; Schmid, C. G.; Chandrasekhar, V.; Day, R. O.; Holmes, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 1408.

(5) Chandrasekhar, V.; Schmid, C. G.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 1050.

(6) Day, R. O.; Chandrasekhar, V.; Kumara Swamy, K. C.; Holmes, J. M.; Burton, S. D.; Holmes, R. R. *Inorg. Chem.* **1988**, *27*, 2887.

(7) Day, R. O.; Holmes, J. M.; Chandrasekhar, V.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 940.

(8) Kumara Swamy, K. C.; Schmid, C. G.; Nadim, H.; Burton, S. D.; Day, R. O.; Holmes, R. R. *Abstracts of Papers*, Third Chemical Congress of North America, Toronto, Canada, June 1988; INOR 508.

(9) A mixture of n-butylstannonic acid (0.962 g, 4.62 mmol) and diphenyl phosphine oxide (0.935 g, 4.62 mmol) in toluene (75 mL) was heated under reflux for 1 h under an atmosphere of nitrogen. A blank reaction of $Ph_2P(O)H$ with sulfur in a toluene–chloroform mixture (3:1) at 60 °C showed the formation of $Ph_2P(S)OH$ (δ (P) = 71.36 ppm). Elemental sulfur (0.147 g, 0.574 mmol) was added to the mixture, and the contents were heated at reflux for 2 h with the azeotropic removal of water. The resulting homogeneous solution was concentrated to ca. 15 mL. A solid material was deposited from this solution upon standing for a day (0.3 g, 17% based on stannonic acid). Crystals suitable for X-ray analysis were grown from a solvent mixture of benzene and dichloromethane (95:5). Anal. Calcd for $C_{96}H_{114}O_{14}P_6S_6Sn_7$ (after removal of solvent of crystallization): C, 42.69; H, 4.22. Found: C, 42.37; H, 4.26. ^1H NMR ($CDCl_3$) 0.67 (t, CH_3, J = 7.1 Hz, 18 H), 1.20 (m, CH_2, 12 H), 1.50–2.20 (br, CH_2—CH_2, 24 H), 6.80–7.80 (m, H_{Ar}, 60 H); ^{31}P NMR ($CDCl_3$, H_3PO_4 ref) 27.28 (s with satellites, ^2J (Sn–O–P) = 130.0 Hz); ^{119}Sn NMR ($CDCl_3$, TMT ref) −467.66 (t, ^2J (Sn–O–P) = 132.0 Hz). We were unable to locate the signal due to the unique tin connected to six sulfur atoms.