Communications to the Editor

Ring-Opening Metathesis Polymerization (ROMP) of Norbornene by a Group VIII Carbene Complex in Protic Media

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Received January 13, 1992

During the past two decades, intense research efforts have enabled an in-depth understanding of the olefin metathesis reaction as catalyzed by early transition metal complexes.[1,2] In contrast, the nature of the intermediates and the reaction mechanism for group VIII transition metal metathesis catalysts remain elusive. Such knowledge is important in view of the promise group VIII metals show in polymerizing a wide variety of functionalized cyclic olefins in protic solvents.[1,3] Highly active late transition metal catalysts should also open the way to the metathesis of functionalized acyclic olefins.[4] Previous studies in our group have focused on the chemistry of highly active, functional-group-tolerant catalysts prepared from aquoruthenium(II) olefin complexes.[3] In these systems, characterization of the catalytic intermediates is difficult due to their very low concentrations and high activity in the reaction mixtures. Although it is reasonable to assume that the active species are ruthenacyclobutanes and ruthenium carbenes (ruthenaolefins),[5] the oxidation state and ligation of these intermediates are not known. Furthermore, the discrete ruthenium carbene complexes that have been isolated to date do not exhibit both metathesis activity and stability to protic/aqueous solvents.[6] We report here the reaction of an Ru(II) complex with a strained olefin to produce a carbene species that polymerizes norbornene in organic media both in the absence and presence of protic/aqueous solvents. In both solvent systems, a stable propagating carbene complex can be observed throughout the course of the polymerization, as has been previously found with titanium, tantalum, tungsten, molybdenum, and ruthenium complexes.[2]

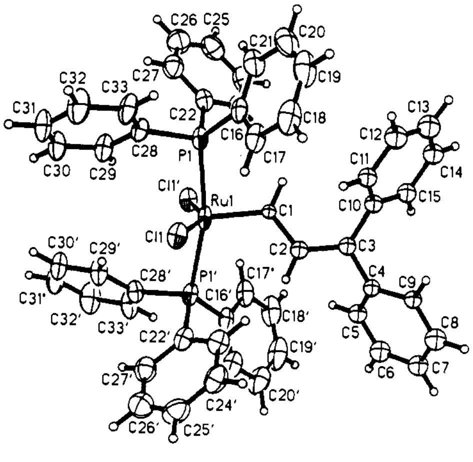
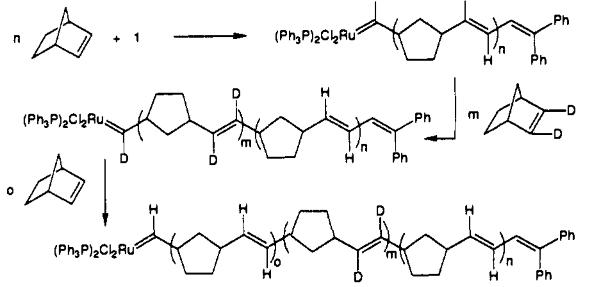
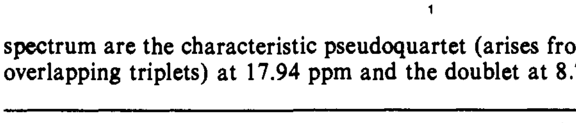


Figure 1. ORTEP diagram of **1**. The thermal ellipsoids are drawn at the 50% probability level.

Scheme I. The Block Copolymerization of 2,3-Dideuterionorbornene and Perprotionorbornene by **1**[16]



The reaction of 3,3-diphenylcyclopropene with either $RuCl_2(PPh_3)_3$ or $RuCl_2(PPh_3)_4$ in a 1:1 mixture of CH_2Cl_2/C_6H_6 produces the carbene complex **1** in essentially quantitative yield (eq 1).[7,8] Key to the structural assignment of **1** from the ¹H NMR



(1)

spectrum are the characteristic pseudoquartet (arises from two overlapping triplets) at 17.94 ppm and the doublet at 8.7 ppm

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(1) For comprehensive accounts on the subject of olefin metathesis, see: (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (b) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience: New York, 1985. (c) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press, Ltd.: New York, 1982; Vol. 8, pp 499–551. (d) Leconte, M.; Basset, J. M.; Quignard, F.; Larroche, C. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, pp 371–420 and references therein.

(2) (a) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, pp 221–283. (b) Feldman, J. R.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1–74. (c) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448–2449. (d) Toreki, R.; Farooq, A.; Schrock, R. R. *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC, August 1990; American Chemical Society: Washington, DC, 1990; INOR 345. (e) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733–742. (f) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721–724. (g) Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583–589. (h) Tumas, W.; Grubbs, R. H. *Science* **1989**, *243*, 907–915. (i) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5384–5385 and references therein.

(3) (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542–7543. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960–961. (c) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules*, in press. (d) France, M. B.; McGrath, D. V.; Paciello, R. A.; Grubbs, R. H. Manuscript in preparation. (e) France, M. B.; Paciello, R. A.; Grubbs, R. H. Manuscript in preparation.

(4) Recently, Schrock and co-workers described several well-defined rhenium alkylidene complexes that catalyze the metathesis of functionalized acyclic olefins. These results are described in refs 2c,d.

(5) Typically, high oxidation state metallaolefins are called alkylidene complexes while low oxidation state analogues are referred to as carbene complexes. The new complex described here does not show all of the characteristics of either of these two classes of complexes. In accord with IUPAC rules, these complexes are all metallaolefins. However, in this communication, the convenient term carbene complex is used.

(6) (a) Casey, C. P.; Palermo, R. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 549–550. (b) Bruce, M. I.; Swincer, A. G.; Thomson, B. J.; Wallis, R. C. *Aust. J. Chem.* **1980**, *33*, 2605–2613. (c) Roper-type Ru carbenes described in ref 11. (d) Zewert, T.; Grubbs, R. H. Unpublished results.

(7) For a detailed synthetic procedure, please refer to the supplementary material. ¹H NMR (C_6D_6): δ 17.94 (pseudoquartet = two overlapping triplets, 1 H, Ru=C*H*, J_{HH} = 10.2 Hz, J_{PH} = 9.7 Hz), 8.33 (d, 1 H, C*H*=CPh₂, J_{HH} = 10.2 Hz). ³¹P NMR (C_6D_6): δ 28.2 (s). ¹³C NMR (CD_2Cl_2): δ 288.9 (t, M=*C*, J_{CP} = 10.4 Hz), 149.9 (t, *C*H=CPh₂, J_{CP} = 11.58 Hz).

(8) The precursor $OsCl_2(PPh_3)_3$ also undergoes a similar reaction to give the Os analogue of **1**.

0002-7863/92/1514-3974$03.00/0

due to H_α and H_β of the vinylcarbene moiety, respectively. Similar ^1H NMR patterns have been observed for the analogous vinylcarbene complexes $Cp_2Ti(PMe_3)(=C(H)CH=CPh_2)$,[9] $Cp_2Zr(PMe_3)(=C(H)CH=CPh_2)$,[9] and $(ArN)WCl_2(P(OMe)_3)_2(=C(H)CH=CPh_2)$,[10] which were prepared by the addition of 3,3-diphenylcyclopropene to the corresponding reduced precursors. Although not directly comparable, the ^{13}C chemical shift of C_α of **1** at 288.9 ppm is in the same range as those found for a variety of known bis(triphenylphosphine)ruthenium(II) and -osmium(II) carbene complexes.[11] The ^{31}P chemical shift at 28.2 ppm for the coordinated triphenylphosphines is similar to that observed at 27.2 ppm for the phosphorous ligands of the recently reported vinylidene complex $(Ph_3P)_2RuCl_2(=C=C(H)^tBu)$.[12] X-ray diffraction data from a single crystal of **1** further confirmed the structural assignment (Figure 1). Unfortunately, the vinylcarbene moiety is disordered about a 2-fold axis, thus preventing an accurate determination of bond lengths and bond angles for this fragment.[13]

In the solid state, complex **1** is stable indefinitely under an inert atmosphere and for several minutes in air. The complex is stable for weeks in organic solvents in the absence of oxygen. Surprisingly, **1** is also stable for several days in CH_2Cl_2/C_6H_6 in the presence of water, alcohol, or a diethyl ether solution of HCl. This unusual stability is consistent with the functional-group tolerance of group VIII metathesis catalysts. As expected, **1** will not undergo Wittig-type reactions with either a ketone or an aldehyde.[14] In preliminary experiments, the ligand environment of **1** was modified by substitution of the chlorides with selected anionic ligands.[15]

Complex **1** polymerizes norbornene in a 1:8 mixture of CH_2Cl_2/C_6H_6 at room temperature to yield polynorbornene.[16] A new signal, attributed to H_α of the propagating carbene, was observed by ^1H NMR spectroscopy at 17.79 ppm.[17] Its identity and stability were confirmed by preparing a block polymer with 2,3-dideuterionorbornene and perprotionorbornene. When 2,3-dideuterionorbornene was added to the propagating species, the new carbene signal vanished and then reappeared when perprotionorbnene was added for the third block (Scheme I). These experiments demonstrate that the active polymer is stable and that chain termination and transfer are extremely slow relative to propagation, thus satisfying the sole criterion for a "living polymer".[18]

Although initiation is slower than propagation, a complete conversion of the parent vinylcarbene to the propagating carbene can be achieved.[19] The propagating carbene, generated from the reaction of **1** with norbornene, is quite stable in the presence of water or ethanol (up to 1000 equiv per catalyst molecule in a 1:9 mixture of CH_2Cl_2/THF; unfortunately, **1** is not soluble in either pure water or alcohol). Protic solvents do not slow down the polymerization activity of the catalyst, and to a first-order approximation, the rate of norbornene polymerization in organic media is comparable to that observed in the presence of protic solvents.

The above observations demonstrate that carbene complexes (metallaolefins) are viable intermediates in the ROMP of bicyclic monomers with group VIII metals, since an isolated, well-characterized ruthenium carbene complex shows all the characteristic reactions that are required for such intermediates. The potential for solvent variation and ligand modification holds great promise for fine-tuning the reactivity of the catalyst.

Acknowledgment. Financial support from the National Science Foundation and Du Pont is gratefully acknowledged. L.K.J. thanks the NSF for an NSF Predoctoral Fellowship. S.T.N. thanks the Department of Defense, Office of Army Research, for an NDSEG Predoctoral Fellowship and Caltech for an Institute Fellowship. Funds for the purchase of the Siemens R3m/V diffractometer system were made available from the National Science Foundation under Grant CHE-85-14495. We thank Dominic V. McGrath for helpful discussions.

Supplementary Material Available: Experimental details and spectroscopic data for complex **1** and its derivatives, additional information regarding the stability of **1**, description of the X-ray diffraction experiment, ORTEP drawings of the molecule showing the disordered components and a stereoview of the molecule, and tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles (19 pages); listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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(9) Binger, P.; Muller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610–611.

(10) Johnson, L. K.; Grubbs, R. H. Manuscript in preparation.

(11) In assigning the oxidation state of these complexes, the carbene moiety was considered to be neutral. See: (a) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *358*, 411–447. (b) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Shepard, W. E. B.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1987**, 563–565. (c) Clark, G. R.; Hodgson, D. J.; Ng, M. M. P.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1552–1554. (d) Wright, A. H.; Roper, W. R. Unpublished results.

(12) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604–9610.

(13) Single crystals of **1** were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution. The molecule crystallized in a monoclinic unit cell, space group $C2/C(C^6_{2h}$; No. 15) with $a = 13.466$ (5) Å, $b = 14.188$ (6) Å, $c = 22.62$ (2) Å, $\beta = 104.50$ (6)°, $V = 4183.0$ (4) Å^3, and $D_{calcd} = 1.41$ g cm^{-3} for $Z = 4$, $T = 178$ K.

(14) For more information on the stability of **1**, please refer to the supplementary material.

(15) For additional details, please see the supplementary material.

(16) At room temperature, 2 mg of **1** polymerizes 70 equiv of norbornene in 0.5 mL of a 1:8 CD_2Cl_2/C_6D_6 solvent mixture in 3 h. The polymer was about 90% trans by ^1H NMR spectroscopy. The classical $RuCl_3$ systems also give a high amount (>90%) of trans polymer.[1a,b]

(17) The parent vinylcarbene shows a quartet at 17.86 ppm in this solvent mixture.

(18) This system is living because the propagating alkylidene is stable on the time scale of the reaction and, as is demonstrated by the blocking experiment, will continue to polymerize quantitatively on addition of further aliquots of monomer several hours after the original amount of norbornene is consumed. See: (a) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Wiley-Interscience: New York, 1968. (b) Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polym. Sci.* **1988**, *86*, 87–143.

(19) For example, when 70 equiv of norbornene was added to **1** in a 1:8 CD_2Cl_2/C_6D_6 solvent mixture, after 50 min only 80% of the parent vinylcarbene was converted to the propagating carbene. Approximately 70% of the monomer was polymerized at this point.

Unprecedented Stereochemistry of the Electrophilic Arylation at Chiral Phosphorus

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Received January 13, 1992

Electrophilic alkylation or arylation reactions of chiral tetracoordinate organophosphorus compounds having a P–H bond are known to proceed with retention of configuration at the phosphorus atom, and to our knowledge, inversion of configuration is unprecedented in this class of reactions.[1] We report herein the first example of inversion in an electrophilic arylation reaction at chiral phosphorus, and in addition, we wish to describe dramatic solvent

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(1) (a) Farnham, W. B.; Murray, R. K.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 5809. (b) Van den Berg, G. R.; Platenburg, D. H. J. M.; Benshop, H. P. *J. Chem. Soc., Chem. Commun.* **1971**, 606. (c) Donohne, J.; Mandel, N.; Farnham, W. B.; Murray, R. K.; Mislow, K.; Benshop, H. P. *J. Chem. Soc., Chem. Commun.* **1972**, 120. (d) Van den Berg, G. R.; Platenburg, D. H. J. M.; Benshop, H. P. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 929. (e) Michalski, J.; Skrzypczynski, Z. *J. Organomet. Chem.* **1975**, *97*, C31. (f) Mikolajczyk, M.; Krzywanski, J. *J. Org. Chem.* **1977**, *42*, 190. (g) Michalski, J.; Skrzypczynski, Z. *J. Chem. Soc., Chem. Commun.* **1977**, 66. (h) Skrzypczynski, Z.; Michalski, J. *J. Org. Chem.* **1988**, *53*, 4549. (i) Zhang, J.; Xu, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1606. (j) Zhang, J.; Xu, Y.; Huang, G.; Guo, H. *Tetrahedron Lett.* **1988**, *29*, 1955. (k) Xu, Y.; Wei, H.; Zhang, J.; Huang, G. *Tetrahedron Lett.* **1989**, *30*, 949.

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