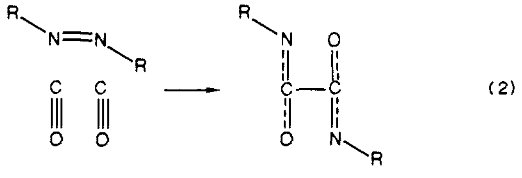

(2)

(1.56 (2) and 1.61 (1) Å vs. a normal 1.42 Å) or its long ortho C–H bonds (stretched by an agostic interaction with samarium), but on the shortest bond in the system, namely, the N=N unit.[4] The utility of this reaction in the derivatization of organic heterocycles[11,20] and in the more general area of organometallic heteroatomic metathesis reactions is under study.

Acknowledgment. We thank the National Science Foundation for support of the research and the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.). We also thank Professor Robert J. Doedens for help with the crystal structure determination.

Supplementary Material Available: Tables of crystal data, bond distances, bond angles, final fractional coordinates, and thermal parameters (5 pages); table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(20) Divalent samarium complexes are receiving increased attention as reagents which can effect unusual transformations on organic substrates.[11,21-25]

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Synthesis, Structure, and Reactions of a Zirconocene-Cyclohexyne Complex

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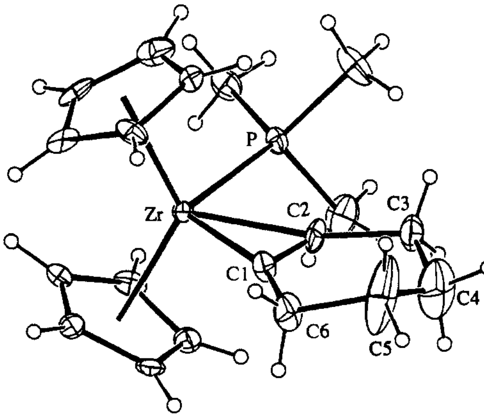
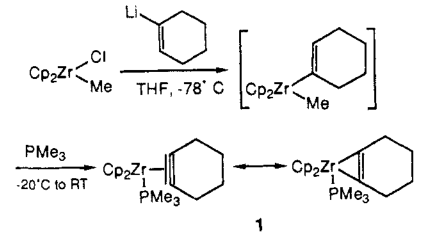
Transition metals have the unique ability to simultaneously stabilize high-energy organic species and to activate them toward selective attack by a variety of chemical reagents. Cyclooctyne is the smallest cycloalkyne to have been prepared in the free state while cycloheptyne and cyclohexyne have been observed as fleeting intermediates by several methods.[1] Several years ago, Bennett and co-workers reported the trapping of in situ generated cyclohexyne and cycloheptyne as their bis(triphenylphosphine)platinum complexes.[2] To date these are the only examples of transition-metal–small-ring cycloalkyne complexes to be reported. We now report the preparation, the X-ray crystal structure, and a number of reactions of the trimethylphosphine adduct of the zirconocene-cyclohexyne complex.



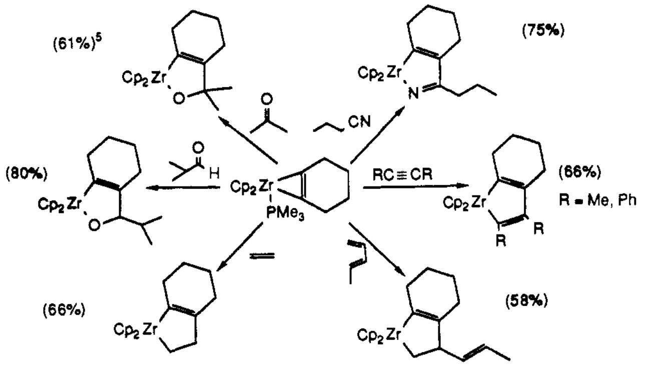
Zr-C1	2 165(13) (Å)
Zr-C2	2 244(12)
C1-C2	1.295(25)
C2-C3	1.532(18)
C1-C6	1.519(19)
Zr-P	2.689(3)
C1-Zr-C2	32.1(0.5) (°)
C1-C2-C3	126.0(1.2)
C6-C1-C2	125.2(1.2)

Figure 1. Molecular structure of 1, with selected bonds and angles.

Scheme I



Scheme II



The trimethylphosphine adduct of the zirconocene-cyclohexyne complex can be prepared as shown in Scheme I. Yields of 60% of **1** as analytically pure material are obtained in this manner, after recrystallization from ether. Compound **1** has been characterized by ^{1}H, ^{13}C, and ^{31}P NMR, elemental analysis, and X-ray crystallography. Each unit cell contains eight molecules, four each of two independent molecules which are nearly identical within experimental error (3σ). Shown in Figure 1 is one of these two molecules, along with important bond angles and distances (average values for the two molecules). Of greatest interest is the carbon-carbon multiple bond length which averages 1.295 (25) Å. This value is essentially identical with that seen in Bennett's platinum complex.[2] As in that case, a significant amount of back-bonding is apparent causing the carbon-carbon bond length to be between that expected for a simple carbon-carbon double[4a] and triple bond.[4b] That the "cyclohexyne" fragment experiences ring strain only to a small extent can also be seen from the C1–C2–C3 and C6–C1–C2 bond angles of 125.2 (1.2)° and 126.0 (1.2)° which deviate only to a small extent from that observed for simple olefins.[4a] Again, this is very similar to what is observed for the platinum complex.

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(4) (a) *Chem. Soc. Spec. Publ.* **1965**, *No. 18*, S14s. (b) *Chem. Soc. Spec. Publ.* **1965**, *No. 18*, S16s.

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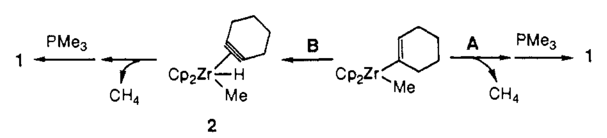
Scheme III



Complex **1** is an air- and moisture-sensitive solid which reacts with a wide variety of unsaturated organic groups as shown in Scheme II. Thus **1** reacts cleanly with nitriles,[6] alkynes,[7] aldehydes, and ketones. Although **1** fails to react with most substituted olefins, it reacts quite cleanly with 1,3-pentadiene (in a completely regiospecific manner) and with ethylene.[8]

It should be noted that if 1-cyclohexenylmethylzirconocene is prepared at low temperature and is treated with nitriles or alkynes at −20 °C, followed by warming to room temperature, metallacyclic products identical with those formed from **1** are observed. However, a similar reaction with isobutyraldehyde led to a complex mixture of products.

Shown in Scheme III are what we feel are the two most likely mechanistic pathways to form **1** from its 1-cyclohexenylmethylzirconocene precursor. In path A, **1** is formed by a C–H activation mechanism with simultaneous production of methane.[9] Such a mechanistic path is completely analogous to that proposed by Erker for the production of a zirconocene–benzyne complex from diphenylzirconocene.[9] An alternate mechanism, shown by path B, would involve a β-hydride elimination to form intermediate **2** followed by reductive elimination of methane. Since **2** would have the zirconium in a d^0 configuration, no back-bonding would be possible to stabilize the cyclohexyne moiety. We feel that **2** would be prohibitively high in energy and we, thus, favor path A.

In summary, we have prepared and structurally characterized the trimethylphosphine adduct of a zirconocene–cyclohexyne complex. We have shown that it structurally more closely resembles a metallacyclopropene rather than a metal–alkyne complex.[10] In addition we have reported on some of the rich reaction chemistry manifested by **1**.

We are currently working on the conversion of the metallacyclic products derived from **1** into synthetically useful organic products and the use of **1** to prepare bimetallic complexes and as an olefin polymerization catalyst. We are also currently attempting to use methodology similiar to that used to prepare **1** to prepare other transition-metal complexes of strained and unstrained systems and we will report on this work in due course.

Acknowledgment. We gratefully acknowledge the support of the National Institutes of Health (GM-34917), the Research Corporation, and Alfred Bader. S.L.B. is the recipient of a Distinguished New Faculty Grant from the Camille & Henry Dreyfus Foundation, Inc., which he gratefully acknowledges. We also thank the Biomedical Research Support Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (NIH Grant S10 RR02243).

Supplementary Material Available: Experimental section containing the preparation of **1** and crystallographic data and procedures, spectroscopic characterization of coupling products, ORTEP diagrams of **1**, and table of final positional and thermal parameters (5 pages); table of structure factors (15 pages). Ordering information is given on any current masthead page.

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(5) Numbers in parentheses refer to isolated yields of purified compounds except for the isobutyraldehyde- and ethylene-derived metallacycles where they refer to yields estimated by ^{1}H NMR.

(6) Buchwald, S. L.; Sayers, A.; Watson, B. T.; Dewan, J. C., submitted for publication in *J. Am. Chem. Soc.*

(7) There are a number of examples of group 4 metallocenes inducing reductive coupling of two alkynes; Cf.: Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422 and references therein. Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

(8) For examples of group 4 metallocene induced reductive coupling of an olefin with an alkyne, Cf.: Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659.

(9) Erker, G. J. *Organomet. Chem.*, **1977**, *134*, 189. C–H activation by d^0 metals is well precedented; for a recent review, Cf.: Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.

(10) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

Rotational Preference in "Cage" Dissociation–Recombinations: Thermal Automerization of Optically Active Methyl *threo*-2,3-Diphenylbutane-2-carboxylate

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First conceived by Franck and Rabinowitch,[1] the "cage" or geminate effect on the recombination of radical pairs is well established, although "the precise definition of the dimensions or other characteristics of this solvent property remains a problem today".[2] In terms of organic chemical phenomenology, the geminate effect relates to those products of radical recombination whose residual amount is irreducible under the influence of efficient traps for *free* radicals.

In this paper, we report the first example of the operation of the "cage" effect on the stereochemical outcome of a thermal epimerization occurring by necessarily single or odd-numbered rotational processes. The original stimulus came from a desire to compare the single rotational preferences which might obtain in a ring of infinite size with those uncovered in the liquid phase, "diradical" automerizations of optically active methyl *threo*-1,2-diphenylcyclopropane-1-carboxylate (R_A = 18)[3] and methyl *threo*-1,2-diphenylcyclopentane-1-carboxylate (R_A = 3.4)[4] to their erythro epimers.[5]

The desired permutation is arranged simply by replacing the rings with two methyl groups! The resulting *acyclic* system of threo configuration is resolved and allowed to automerize thermally to its erythro epimer, in which the preference of one radical component to rotate over the other can be deduced unequivocally (Figure 1). First shedding of light on rotation in a "cage" came from the definitive, independent works of Kopecky and Gillan[7] and Greene et al.[8] on the generation of α-phenylethyl radicals from optically active azo precursors in the presence of scavengers. Both groups observed some retention of activity. The probability of rotation (x = 0.50 corresponds to random) occurring prior to geminate recombination in the work of Greene et al. ($x = 0.44_7$), using 2-methyl-2-nitrosopropane (1.15 M) as scavenger in benzene (Figure 2), compares well with that ($x = 0.43_6$) found by Kopecky and Gillan, using butanethiol (1.2 M) also in benzene.

Complications stemming from the generation of two radicals in a ménage à trois (N$_2$ and CO$_2$ in several examples[2]) were avoided in a bond-breaking, bond-making, pas de deux sequence developed by Singer et al.[9] In their ingenious, pioneering example,

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(1) Franck, J.; Rabinowitch, E. *Trans. Faraday Soc.* **1934**, *30*, 120–131.

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(5) These processes are effected by internal rotation of the benzylic component or the carbomethoxyphenyl component and are defined quantitatively by the thermodynamic ratio, R_A, of the single rotational propensities.[6]

(6) Doering, W. v. E.; Sachdev, K. *J. Am. Chem. Soc.* **1974**, *96*, 1168–1187.

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(8) Greene, F. D.; Berwick, M. A.; Stowell, T. C. *J. Am. Chem. Soc.* **1970**, *92*, 867–874.

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