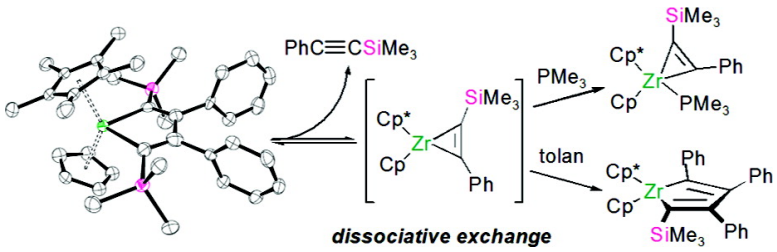
Article

Mechanism of Reversible Alkyne Coupling at Zirconocene: Ancillary Ligand Effects

Adam D. Miller, Jennifer L. McBee, and T. Don Tilley

J. Am. Chem. Soc., **2008**, 130 (14), 4992-4999 • DOI: 10.1021/ja800025u



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
ARTICLES
Published on Web 03/13/2008

Mechanism of Reversible Alkyne Coupling at Zirconocene: Ancillary Ligand Effects

Adam D. Miller, Jennifer L. McBee, and T. Don Tilley*

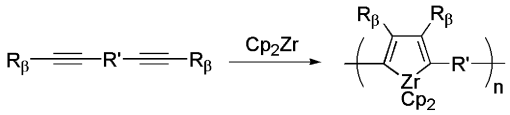
Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1460

Received January 2, 2008; E-mail: tdtilley@berkeley.edu

Abstract: The mechanism of reversible alkyne coupling at zirconium was investigated by examination of the kinetics of zirconacyclopentadiene cleavage to produce free alkynes. The zirconacyclopentadiene rings studied possess trimethylsilyl substituents in the α-positions, and the ancillary Cp_2, $Me_2C(\eta^5\text{-}C_5H_4)_2$, and CpCp* (Cp* = η^5-C_5Me_5) bis(cyclopentadienyl) ligand sets were employed. Fragmentation of the zirconacyclopentadiene ring in $Cp_2Zr[2,5\text{-}(Me_3Si)_2\text{-}3,4\text{-}Ph_2C_4]$ with PMe_3, to produce $Cp_2Zr(\eta^2\text{-}PhC{\equiv}CSiMe_3)(PMe_3)$ and free $PhC{\equiv}CSiMe_3$, is first-order in initial zirconacycle concentration and zero-order in incoming phosphine ($k_{obs} = 1.4(2) \times 10^{-5}$ s^{-1} at 22 °C), and the activation parameters determined by an Eyring analysis ($\Delta H^{\ddagger} = 28(2)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 14(4)$ eu) are consistent with a dissociative mechanism. The analogous reaction of the *ansa*-bridged complex $Me_2C(\eta^5\text{-}C_5H_4)_2Zr[2,5\text{-}(Me_3Si)_2\text{-}3,4\text{-}Ph_2C_4]$ is 100 times faster than that for the corresponding Cp_2 complex, while the corresponding CpCp* complex reacts 20 times slower than the Cp_2 derivative. These rates appear to be largely influenced by the steric properties of the ancillary ligands.

Introduction

The reductive coupling of alkynes by zirconocene is an important carbon−carbon bond-forming reaction.[1−3] The resulting zirconacyclopentadienes are useful precursors to a wide range of organic molecules including (for example) dienes,[4] arenes,[5−10] cyclopentadienes,[11−13] thiophenes,[14,15] phospholes,[16] thiophene oxides,[17] and bicyclic compounds.[18] We have employed this reaction for the development of efficient synthetic routes to polymers,[19−21] oligomers,[17,22] and macrocycles,[23−30] via the coupling of diynes of the type RC≡C−R′−C≡CR containing rigid spacer groups (R′). These investigations have shown that the nature of the alkyne substituents is critical in determining the structure of the resulting coupled products. One critical factor relates to the propensity of a substituent to adopt the α- (−2 and −5) or β- (−3 and −4) positions of a zirconacyclopentadiene ring. For example, a β-directing alkyne substituent (R_β), which forces the carbon it is bound to into the β-position of the zirconacyclopentadiene ring, will incorporate the spacer of a diyne (R′) into the backbone of an oligomer or polymer (eq 1). The regioselectivity associated with alkyne coupling also plays a role in the formation of macrocycles, but a more important requirement in this case is that the alkyne substituents promote reversibility for zirconacyclopentadiene formation.[30]

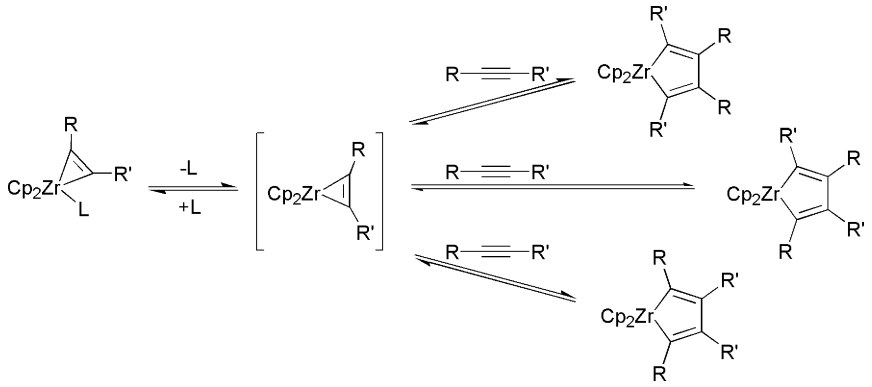


(1)

(1) Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755−769.
(2) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696−1701.
(3) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058.
(4) Lucht, B. L.; Tilley, T. D. *Chem. Commun.* **1998**, 1645−1646.
(5) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154−5155.
(6) Takahashi, T.; Ishikawa, M.; Huo, S. Q. *J. Am. Chem. Soc.* **2002**, *124*, 388−389.
(7) Takahashi, T.; Kotora, M.; Xi, Z. F. *J. Chem. Soc., Chem. Commun.* **1995**, 361−362.
(8) Takahashi, T.; Li, Y. Z.; Stepnicka, P.; Kitamura, M.; Liu, Y. J.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576−582.
(9) Takahashi, T.; Tsai, F. Y.; Li, Y. Z.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1999**, *121*, 11093−11100.
(10) Takahashi, T.; Xi, Z. F.; Yamazaki, A.; Liu, Y. H.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672−1680.
(11) Takahashi, T.; Sun, W. H.; Xi, C. J.; Kotora, M. *Chem. Commun.* **1997**, 2069−2070.
(12) Kotora, M.; Xi, C. J.; Takahashi, T. *Tetrahedron Lett.* **1998**, *39*, 4321−4324.
(13) Xi, Z.; Li, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2950−2952.
(14) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880−1889.
(15) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310−2312.
(16) Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulaszi, L.; Reau, R. *Chem.−Eur. J.* **2001**, *7*, 4222−4236.
(17) Jiang, B. W.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9744−9745.
(18) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788−2796.
(19) Lucht, B. L.; Buretea, M. A.; Tilley, T. D. *Organometallics* **2000**, *19*, 3469−3475.
(20) Lucht, B. L.; Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 4354−4365.
(21) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566−5569.
(22) Suh, M. C.; Jiang, B. W.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 2870−2873.
(23) Mao, S. S. H.; Liu, F. Q.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 1193−1206.
(24) Schafer, L. L.; Nitschke, J. R.; Mao, S. S. H.; Liu, F. Q.; Harder, G.; Haufe, M.; Tilley, T. D. *Chem.−Eur. J.* **2002**, *8*, 74−83.
(25) Schafer, L. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 2683−2684.
(26) Nitschke, J. R.; Zurcher, S.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 10345−10352.
(27) Nitschke, J. R.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 10183−10190.
(28) Nitschke, J. R.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2001**, *40*, 2142−2145.
(29) Liu, F. Q.; Harder, G.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 3271−3272.
(30) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5365−5366.

10.1021/ja800025u CCC: $40.75

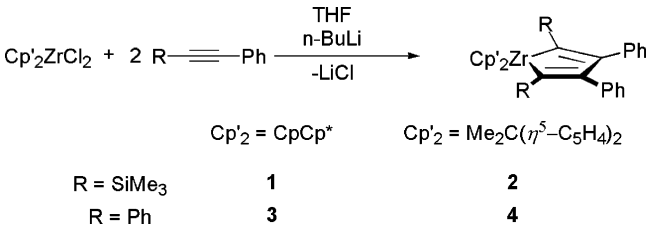
Scheme 1



It is well known that certain sterically demanding alkyne substituents, such as trimethylsilyl,[31] *tert*-butyl,[18,32] and diphenylphosphino[33] groups, direct alkyne couplings such that they adopt the α-positions of the zirconacyclopentadiene ring. These groups also promote reversibility for alkyne couplings and give labile metallacycles.[34,35] Thus, zirconocene couplings of diynes of the type $Me_3SiC{\equiv}C{-}R'{-}C{\equiv}CSiMe_3$ are particularly useful in the synthesis of macrocycles.[24] On the other hand, electron-withdrawing alkyne substituents can preferentially adopt the β-positions of a zirconacyclopentadiene ring, and this has been explained in terms of charge distributions in the transition state for alkyne coupling. This transition state has a highly unsymmetrical structure according to DFT calculations and is best described as an alkyne adduct of a zirconacyclopropene.[36]

Although the synthetic utility of the reductive coupling of alkynes by zirconocene is firmly established, there has been little investigation into the mechanism of such couplings. In addition, the possible effects of alternative ancillary ligand sets, on (for example) regioselectivity, reversibility, and coupling rates, have yet to be determined. Characterization of the mechanism is necessary to gain a better understanding of the factors that influence the course of alkyne couplings at zirconium. Kinetic and mechanistic investigations of zirconocene-mediated alkyne couplings are inherently difficult, given the high rates of these reactions, the uncertainty in the exact nature of the zirconocene species that initiate the coupling, and the fact that intermediate species (i.e., zirconacyclopropenes) are fleeting and difficult to observe. To the best of our knowledge, zirconacyclopropenes containing the Cp_2Zr moiety have been isolated only as base adducts;[34,37−39] however, related complexes with substituted cyclopentadienyl ligands of the type $C_5H_{5-n}Me_n$ ($n = 2-5$) are known.[40,41]

Scheme 2



	Cp'$_2$ = CpCp*	Cp'$_2$ = Me$_2$C(η^5–C$_5$H$_4$)$_2$
R = SiMe$_3$	**1**	**2**
R = Ph	**3**	**4**

It has been assumed that alkyne coupling occurs in a stepwise manner, and evidence for this exists in the fact that some zirconacyclopentadienes react with a Lewis base to eliminate 1 equiv of alkyne to form a base-stabilized zirconacyclopropene (Scheme 1).[34] Thus, it seemed possible to probe the mechanism of alkyne coupling by examining the reverse process, and this approach was taken in the research described herein. These mechanistic investigations were used to probe ancillary ligand effects on this chemistry, and for this purpose the Cp_2, $Me_2C(\eta^5\text{-}C_5H_4)_2$, and CpCp* (Cp* = η^5-C_5Me_5) bis(cyclopentadienyl) ligand sets were employed. For each zirconocene system, kinetic and mechanistic investigations targeted the fragmentation of a zirconacyclopentadiene, the microscopic reverse of alkyne coupling (Scheme 1, L = PMe_3). X-ray structure determinations have also contributed to the mechanistic picture that emerges from these studies.

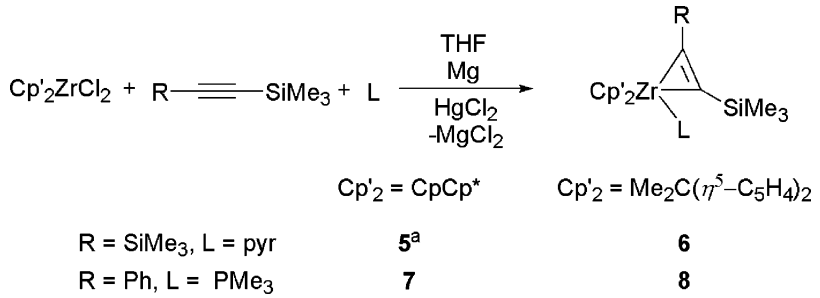
Results and Discussion

Since trimethylsilyl substituents are known to enhance reversibility for zirconocene-mediated alkyne couplings, investigations targeted 2,5-bis(trimethylsilyl)-3,4-diphenylzirconacyclopentadiene derivatives. To explore the influence of ancillary ligands on zirconocene coupling, various bis(cyclopentadienyl) substituents were also examined. Zirconacycles containing the ancillary ligands $Me_2C(\eta^5\text{-}C_5H_4)_2$ and CpCp* are of particular interest since most reported zirconacyclopentadienes feature the Cp_2 or Cp^*_2 ligand sets.[42−46]

Synthesis of Zirconacyclopentadiene and Zirconacyclopropene Complexes. The starting compounds used in this study

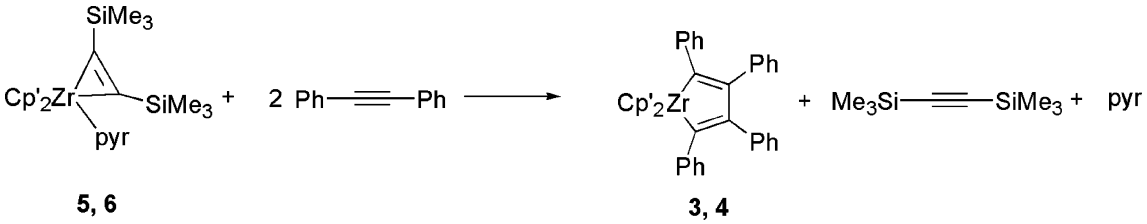
(31) Erker, G.; Zwettler, R.; Kruger, C.; Hylakryspin, I.; Gleiter, R. *Organometallics* **1990**, *9*, 524−530.
(32) Hara, R.; Xi, Z. F.; Kotora, M.; Xi, C. J.; Takahashi, T. *Chem. Lett.* **1996**, 1003−1004.
(33) Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J. P.; Dupuis, L.; Pirio, N.; Meunier, P. *Chem. Commun.* **1997**, 279−280.
(34) Erker, G.; Zwettler, R. *J. Organomet. Chem.* **1991**, *409*, 179−188.
(35) Takahashi, T.; Kotora, M.; Hara, R.; Xi, Z. F. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2591−2602.
(36) Johnson, S. A.; Liu, F. Q.; Suh, M. C.; Zurcher, S.; Haufe, M.; Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 4199−4211.
(37) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623−626.
(38) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544−2546.
(39) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Gorls, H.; Burlakov, V. V.; Shur, V. B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 77−83.
(40) Hiller, J.; Thewalt, U.; Polasek, M.; Petrusova, L.; Varga, V.; Sedmera, P.; Mach, K. *Organometallics* **1996**, *15*, 3752−3759.
(41) List, A. K.; Koo, K.; Rheingold, A. L.; Hillhouse, G. L. *Inorg. Chim. Acta* **1998**, *270*, 399−404.
(42) Bradley, C. A.; Keresztes, I.; Lobkovsky, E.; Young, V. G.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 16937−16950.
(43) Fernandez, F. J.; Galakhov, M. V.; Royo, P. *J. Organomet. Chem.* **2000**, *594*, 147−153.
(44) Legrand, C.; Meunier, P.; Petersen, J. L.; Tavares, P.; Bodiguel, J.; Gautheron, B.; Dousse, G. *Organometallics* **1995**, *14*, 162−169.
(45) Basta, R.; Harvey, B. G.; Arif, A. M.; Ernst, R. D. *Inorg. Chim. Acta* **2004**, *357*, 3883−3888.
(46) Kulsomphob, V.; Harvey, B. G.; Arif, A. M.; Ernst, R. D. *Inorg. Chim. Acta* **2002**, *334*, 17−24.

Scheme 3

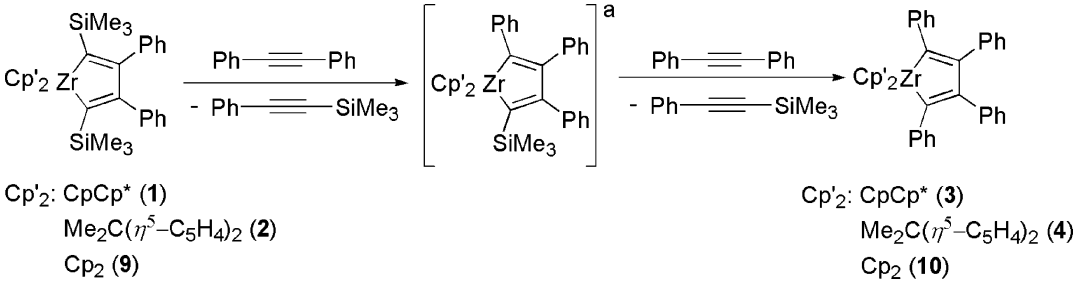


[a] The reducing agent was *n*-BuLi rather than $Mg/HgCl_2$.

Scheme 4



Scheme 5



[a] This intermediate was observed only for zirconacycle **1**.

were synthesized by reduction of the appropriate zirconocene dichloride in the presence of an alkyne, with either butyl lithium in THF (Negishi protocol)[47] or magnesium amalgam[48] as the reductant. Zirconacyclopentadienes **1**−**4** were prepared by generation of the zirconocene synthon via the method of Negishi in 28−68% yields (Scheme 2). A similar method was used to obtain the zirconacyclopropene complex CpCp*Zr(pyr)(η^2-$Me_3SiC{\equiv}CSiMe_3$) (**5**), which was expected to serve as a convenient synthon for the zirconocene CpCp*Zr. This compound is related to Rosenthal's $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$,[39] which is a mild and efficient synthetic source of zirconocene.[26] Synthesis of zirconacyclopropenes **6**−**8** typically required a different reduction procedure (Scheme 3). These complexes were obtained in 29−51% yields via treatment of the zirconocene dichloride with magnesium powder and mercury chloride in THF at −78 °C, followed by addition of the alkyne and then the appropriate Lewis base (pyridine or PMe_3). All new compounds were obtained as analytically pure solids that were fully characterized by ^1H, ^{13}C, and/or ^{31}P NMR spectroscopy.

Reactions of Zirconocene Complexes with Alkynes. To evaluate the utility of compounds **5** and **6**, the analogues to Rosenthal's $Cp_2Zr(pyr)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$, as precursors to zirconacyclopentadiene complexes, their reactions with alkynes were examined. The reaction of the CpCp* compound **5** with 2 equiv of PhC≡CPh (tolan) in benzene-d_6 occurred over 24 h at 75 °C, to give zirconacyclopentadiene **3** in quantitative yield (by ^1H NMR spectroscopy; Scheme 4). During the course of this reaction, two intermediates were observed by ^1H NMR spectroscopy with sets of CpCp* resonances at 5.73, 1.65 ppm and 5.58, 1.55 ppm. These spectra also contained new resonances for coordinated pyridine and bound $Me_3SiC{\equiv}CSiMe_3$, implying that these intermediates are CpCp*Zr(η^2-PhC≡CPh)(pyr) and CpCp*Zr[2,3-$(Me_3Si)_2$-4,5-Ph_2C_4], respectively. In contrast, *ansa* complex **6** was converted cleanly to zirconacycle **4** within only 30 min at ambient temperature under analogous reaction conditions.

The labile complex Cp_2Zr[2,5-$(Me_3Si)_2$-3,4-Ph_2C_4] (**9**) readily undergoes substitution by alkynes less sterically encumbered than $Me_3SiC{\equiv}CPh$ (e.g., tolan) to form zirconacyclopentadienes derived from the newly introduced alkyne, with liberation of 2 equiv of $Me_3SiC{\equiv}CPh$.[32,35] To compare the reactivities of **1**, **2**, and **9** in this type of alkyne-substitution process, slightly more than 2 equiv of tolan in benzene-d_6 were added to each complex, and the reactions were monitored by NMR spectroscopy. The *ansa* complex **2** readily underwent alkyne ligand exchange with tolan (2.1 equiv) at ambient temperature, and complete conversion to **4** was observed after 1 h (Scheme 5). Compound **9** smoothly reacted with 2.1 equiv of tolan at 80 °C to yield the tetraphenylzirconacyclopentadiene (**10**) in less than 1 h. By comparison, only 50% of the CpCp* complex **1** had reacted

(47) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829−2832.
(48) Thanedar, S.; Farona, M. F. *J. Organomet. Chem.* **1982**, *235*, 65−68.

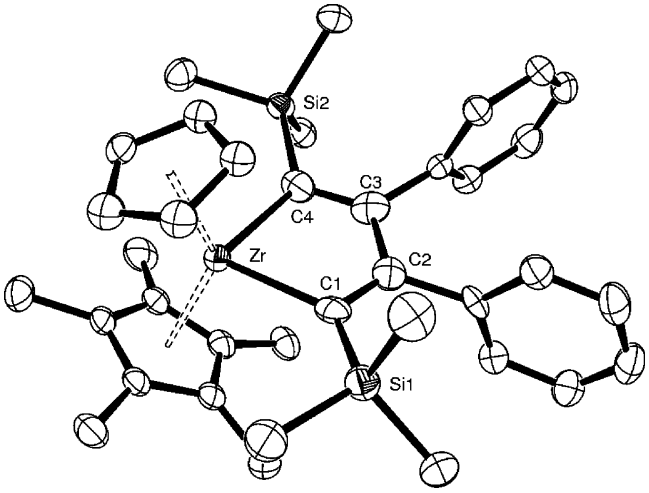


Figure 1. ORTEP depiction of the solid-state molecular structure of **1**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn with 50% probabilities. Compound **1** was crystallized in the $P\bar{1}$ space group with the following refinement parameters: R1 = 0.0334, wR2 = 0.0930, and GOF = 1.086. Selected bond lengths (Å), bond angles (°): Zr−C1, 2.266(3); C1−C2, 1.360(4); C2−C3, 1.523(4); C2−C1−Si1, 121.8(2); Cp_{cent}−Zr−Cp_{cent}, 135.4.

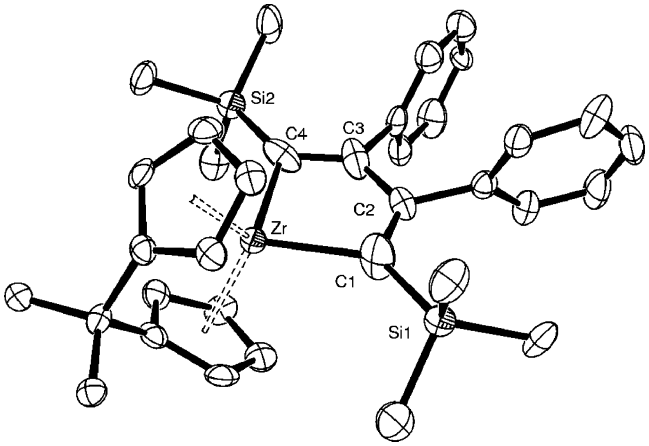


Figure 2. ORTEP depiction of the solid-state molecular structure of **2**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn with 50% probabilities. Compound **2** was crystallized in the $P\bar{1}$ space group with the following refinement parameters: R1 = 0.0402, wR2 = 0.0825, and GOF = 0.821. Selected bond lengths (Å), bond angles (°): Zr−C1, 2.243(4); C1−C2, 1.348(5); C2−C3, 1.538(6); C2−C1−Si1, 125.5(3); Cp_{cent}−Zr−Cp_{cent}, 115.6.

under the same conditions, and by ^{1}H NMR spectroscopy the main product appears to be the unsymmetrical zirconacyclopentadiene formed by a single alkyne substitution. This product exhibits resonances at −0.04 (α-$SiMe_3$), 1.76 (Cp*), and 6.37 (Cp) ppm. Increasing the temperature to 100 °C resulted in formation of the expected zirconacycle **3** over 14 h. Thus, the influence of ancillary ligands on the rates of these alkyne substitution reactions follows the pattern $Me_2C(C_5H_4)_2$ > Cp_2 > CpCp*.

Structural Studies. The molecular structures of zirconacyclopentadienes **1** and **2** were determined by single-crystal X-ray crystallography, and ORTEP diagrams[49] of each are shown in Figures 1 and 2. The structure of compound **9** was previously reported by Erker and co-workers.[31] The *ansa*-bridged zirconacyclopentadiene **2** exhibits the smallest angle associated with binding of the bis(cyclopentadienyl) ligand set (Cp_{cent}−Zr−Cp_{cent}; 115.6°), which results in a more exposed, less sterically congested zirconium center. The constraint imposed by the *ansa*-Me_2C bridge should result in less orbital overlap between the cyclopentadienyl ring systems and zirconium, such that this ligand set is a relatively poor electron donor.[50] The presence of a Cp* ligand might be expected to increase the Cp_{cent}−Zr−Cp_{cent}, but the steric influence of the −$SiMe_3$ groups in the α-positions of the metallacycle acts to counter this effect, such that this angle in **1** (121.8°) is less than that in the Cp_2 analogue **9** (124.4°). Thus, compound **1** may be viewed as possessing a considerably more crowded metal center and the most electron-donating ligand set. The relief of steric pressure around the metal center associated with the *ansa* bridge of **2** results in the shortest distance from the metal to the α-carbon of the cyclopentadiene ring (Zr−C1, 2.243(4) Å). For comparison, the corresponding distances in **1** and **9** are 2.266(3) and 2.264(2) Å, respectively.

Kinetic Studies of Alkyne Substitution. To quantify differences in rates of alkyne substitution (*vide supra*), a kinetic study was initiated. It was previously reported that Cp_2Zr[2,5-$(Me_3Si)_2$-3,4-Ph_2C_4] readily fragments to form a zirconacyclopropene, with liberation of 1 equiv of trimethylsilylphenylacetylene in the presence of a donor ligand such as PMe_3.[34] Similarly, treatment of the zirconacycles **1**, **2**, and **9** with 10 equiv of PMe_3 at ambient temperature in benzene-d_6 resulted in quantitative formation of zirconacyclopropenes **7**, **8**, and **11**, respectively, with release of 1 equiv of free $Me_3SiC{\equiv}CPh$ (by ^{1}H NMR spectroscopy). Under these pseudo-first-order conditions, data were collected for up to five half-lives and the products were identified by comparisons to the independently synthesized compounds described above, or to those previously reported in the literature.[34] The observed, pseudo-first-order rate constants are summarized in Scheme 6. The rate constant observed for the fragmentation of **9** with excess PMe_3 (10 equiv) at 50 °C was found to be $k_{obs} = 1.08(5) \times 10^{-3}$ s^{-1}. This value is similar to that for the rate of substitution of 1 equiv of $Me_3SiC{\equiv}CPh$ in **9** in the presence of an excess of tolan (10 equiv) at 50 °C ($k_{obs} = 0.88(3) \times 10^{-3}$ s^{-1}). The substitution of $Me_3SiC{\equiv}CPh$ is expected to occur in a sequential process to first form the unsymmetrical Cp_2Zr[2-(Me_3Si)-3,4,5-Ph_3C_4], which then undergoes a second substitution to form the tetraphenylzirconacyclopentadiene (**10**). The formation of Cp_2Zr[2-(Me_3Si)-3,4,5-Ph_3C_4] is supported by ^{1}H NMR spectra which contain resonances for an intermediate species with −$SiMe_3$ (−0.14 ppm) and Cp (6.14 ppm) groups. The similarity in the substitution rates of $Me_3SiC{\equiv}CPh$ with either PMe_3 or tolan suggests that the two substitution reactions proceed by related mechanisms (Scheme 1).

It is believed that the initial reaction steps of zirconocene-promoted alkyne coupling involve the formation of a transient 16-electron monoalkyne complex.[3,36,51,52] The intermediate zirconacyclopropene then rapidly adds a second equivalent of alkyne to give the zirconacylopentadiene. Given that alkyne substitution by PMe_3 in zirconacyclopentadienes represents a process very similar to the reverse of alkyne coupling, it seemed that this reaction might occur via a reversible ring fragmentation to generate a zirconacyclopropene followed by trapping with

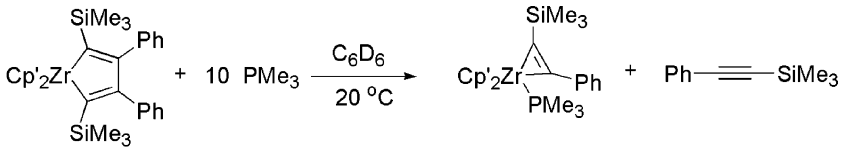
(49) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(50) Lee, H.; Desrosiers, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255−3256.

(51) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870−2874.

(52) Imabayashi, T.; Fujiwara, Y.; Nakao, Y.; Sato, H.; Sakaki, S. *Organometallics* **2005**, *24*, 2129−2140.

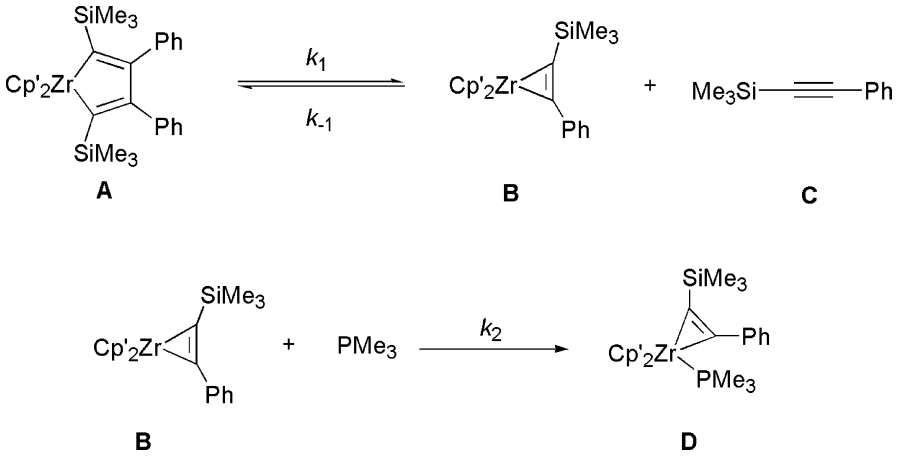
Scheme 6



Cp'$_2$: CpCp* (**1**)
$Me_2C(\eta^5\text{–}C_5H_4)_2$ (**2**)
Cp_2 (**9**)

Cp'$_2$: CpCp* (**7**), k_{obs} = 6.5(7) x 10^{-7} s^{-1}
$Me_2C(\eta^5\text{–}C_5H_4)_2$ (**8**), k_{obs} = 1.4(1) x 10^{-3} s^{-1}
Cp_2 (**11**), k_{obs} = 1.4(2) x 10^{-5} s^{-1}

Scheme 7



PMe_3 (Scheme 7). The first step of this mechanism is consistent with the observed first-order dependence on the concentration of the starting zirconacyclopentadiene, exhibited by the reactions of **1**, **2**, and **9** with excess PMe_3 (10 equiv). Attempts to determine the rate dependence on the concentration of PMe_3 involved monitoring the kinetics of reactions of **1**, **2**, and **9** with varying PMe_3 concentrations (see the Supporting Information for details). For these reactions, second-order kinetics were not observed and the reaction rates were found to be insensitive to the phosphine concentration. Additional mechanistic insight was gained by measuring the activation parameters for the alkyne substitution in zirconacycle **9** by PMe_3. An Eyring plot of the rate data for the temperature range of 22−72 °C (Figure 3) provided the activation parameters $\Delta H^{\ddagger} = 28(2)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 14(4)$ eu. The significantly positive entropy of activation and the observed rate law strongly indicate the operation of a dissociative mechanism for the alkyne/PMe_3 exchange.[53]

Attempts to measure k_1 (Scheme 7) independently, as a verification of the results obtained under pseudo-first-order conditions, involved 2-D EXSY NMR experiments designed to measure the exchange rate of free $Me_3SiC{\equiv}CPh$ with the bound alkyne of zirconacyclopentadiene **A**. However, this exchange could not be observed below the decomposition temperature of **9** (ca. 75 °C).

The observed first-order rate law, k_{obs}[zirconocene], is consistent with the two-step mechanism of Scheme 7, with alkyne dissociation as the rate-limiting step. For a dissociative mechanism, it might be expected that added alkyne ($PhC{\equiv}CSiMe_3$, **C**) would suppress the rate of substitution. However, with **C**/PMe_3 ratios of 3, 9, 42, and 55, substitution reactions of zirconacycle **9** proceeded at similar rates. This, along with the observation that the rate constant does not vary with changes in the concentration of PMe_3, suggests that the rate constant for trapping with PMe_3 (k_2) must be extremely large.

The above mechanistic studies have established that the rates of alkyne substitution by PMe_3 in a zirconacyclopentadiene are first-order in zirconacycle concentration and have no observed dependence on the concentration of PMe_3. The generality of this dissociative mechanism, in which zirconacyclopentadiene fragmentation is the rate-determining step, is supported by the close similarity in rates for alkyne substitutions with PMe_3 or tolan, suggesting that both reactions occur through the same zirconacyclopropene intermediate. These results have implications for the reductive coupling of alkynes by the zirconocene

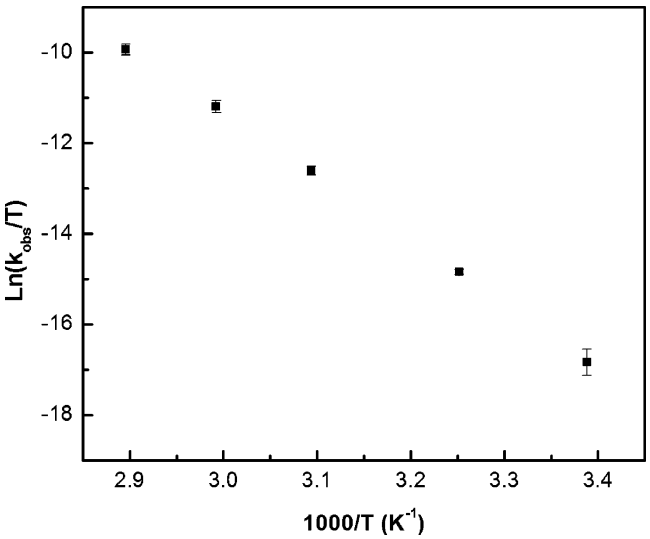
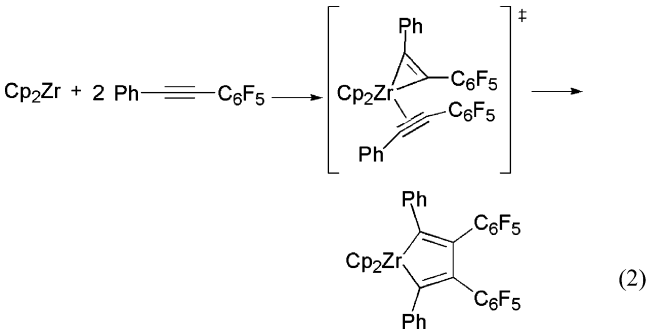


Figure 3. Eyring plot for the rate of disappearance of **9** over the temperature range from 22 to 72 °C.

(53) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms;* Brooks/Cole Pub. Co.: Monterey, CA, 1985.

fragment, which presumably goes through the same zirconacyclopropene intermediate.

Influence of Ancillary Ligands on Alkyne Coupling. The observed first-order rate constants for the fragmentations of zirconacyclopentadienes with PMe_3 depend very much on the nature of the ancillary bis(cyclopentadienyl) ligand sets, with the ratio of relative rates being 0.046:1:100 (CpCp*/Cp_2/$Me_2C(\eta^5\text{-}C_5H_4)_2$). Thus, the rate is greater with less sterically demanding and less electron-donating ancillary ligands. The influence of these ligands on the dissociative substitutions of alkynes can be rationalized in terms of the mechanism in Scheme 7, which is consistent with the investigations described above, and with computational studies.[36,52,54] The transition state for alkyne coupling at zirconocene has been calculated for $Cp_2Zr[2,5\text{-}Ph_2\text{-}3,4\text{-}(C_6F_5)_2]$[36] (eq 2). These results indicate that the transition state is highly unsymmetrical, with one alkyne strongly bonded to zirconium to give a zirconacyclopropene structure (C−C bond length: 1.296 Å) while the other alkyne is very weakly bonded with little perturbation of its geometry (C−C bond length: 1.236 Å). As the coupling reaction proceeds, the more activated alkyne moves into the wedge formed by the two Cp ligands, and repulsive steric interactions between the Cp groups and the phenyl ring of this alkyne ligand are further intensified by a "pivoting" of this alkyne as the zirconacyclopentadiene ring forms. The geometric changes associated with this coupling result in a constriction of the $Cp_{cent}-Zr-Cp_{cent}$ angle, as indicated by the relatively small value calculated for the transition state (128.7°) vs that observed for $Cp_2Zr[2,5\text{-}Ph_2\text{-}3,4\text{-}(C_6F_5)_2]$ (136.6°). Thus, bis(cyclopentadienyl) ligand sets that enforce a smaller $Cp_{cent}-Zr-Cp_{cent}$ angle, such as $Me_2C(\eta^5\text{-}C_5H_4)_2$, should lower the transition-state energy. On the other hand, the sterically hindered Cp* ligand prevents a significant reduction in the $Cp_{cent}-Zr-Cp_{cent}$ angle and leads to a higher transition-state energy.



(2)

The electronic properties of the bis(cyclopentadienyl) ligand set may also play an important role in influencing the rate of alkyne coupling. Theoretical calculations suggest that electron-donating ancillary ligands stabilize the transition state for alkyne−alkyne coupling at zirconium.[52] Therefore, more electron-donating bis(cyclopentadienyl) ligand sets might be expected to increase the rate of alkyne coupling. The Cp* ligand is relatively electron-donating, and calculations on the Cp^*_2Zr fragment indicate that the Cp* ligands raise the HOMO energy of this fragment compared to that of Cp_2Zr.[54] This has also been experimentally confirmed by the lower energy carbonyl stretches of $Cp^*_2Zr(CO)_2$ ($\nu(CO)_{avg}$ = 1899.5 vs 1932.0 cm^{-1} for $Cp_2Zr(CO)_2$), which indicate greater back-donation in these compounds.[54] The $Me_2C(\eta^5\text{-}C_5H_4)_2Zr$ fragment appears to have a slightly destabilized HOMO compared to that of the Cp_2Zr fragment, despite the fact that the carbonyl stretching frequencies in $Me_2C(\eta^5\text{-}C_5H_4)_2Zr(CO)_2$ are slightly higher in energy ($\nu(CO)_{avg}$ = 1935.0 cm^{-1}).[54] Thus, on the basis of the theoretical results cited above, the influence of ancillary ligand sets on the rates of alkyne coupling should be ordered such that CpCp* > Cp_2 > $Me_2C(\eta^5\text{-}C_5H_4)_2$. The experimental results presented above, however, reflect the opposite trend, with the fastest rate for alkyne coupling being associated with the $Me_2C(\eta^5\text{-}C_5H_4)_2Zr$ fragment. This indicates that steric factors override electronic influences in these coupling reactions.

Conclusions

Given the synthetic utility of reversible alkyne couplings involving zirconacyclopentadienes,[23−30,32,34] it is important to develop a detailed understanding of the mechanism of this process and the manner in which steric and electronic factors influence reactivity. The results reported here, which represent the first kinetic and mechanistic studies of this reaction, provide insights into how these couplings occur. Although the kinetic studies focused on the fragmentation of zirconacyclopentadienes (the reverse of alkyne coupling), a number of conclusions regarding the mechanism of alkyne coupling can be made. Consistent with previous computational studies, the experimental results point to stepwise activations of the two alkynes. Thus, the dissociative nature of the zirconacycle fragmentation is consistent with alkyne couplings that occur via reaction of the second alkyne with a zirconacyclopropene complex.

The kinetic analysis described here offers an opportunity to probe steric and electronic effects on alkyne couplings at zirconium. Kinetic and mechanistic information is very useful for the development of an understanding of factors that control regiochemistry and the supramolecular chemistry associated with reversible couplings.[19−35] Steric effects dominate the rate of alkyne substitution in zirconacyclopentadienes, but not in the manner that might be expected. Thus, sterically crowded zirconacyclopentadienes do not eliminate alkyne more rapidly. The least sterically demanding ancillary ligand set, $Me_2C(\eta^5\text{-}C_5H_4)_2$, leads to the fastest rate for alkyne substitution, and the more sterically demanding CpCp* ligands decrease the rate for alkyne substitution (relative to Cp_2). Combined with structural[31] and computational[36,52] studies on these coupling reactions, the results indicate that facile alkyne couplings at a zirconocene center require considerable space in the plane bisecting the cyclopentadienyl ligands to accommodate necessary pivoting motions for the two alkyne ligands. This information regarding the influence of ancillary ligands will be useful for future synthetic efforts that employ new alkyne substituents in regioselective and/or reversible couplings to small molecules, oligomers, polymers, macrocycles, and cages.

Experimental Section

General Procedures. All manipulations were performed under a dry, nitrogen atmosphere using standard Schlenk techniques or a nitrogen-filled glovebox. Dry, oxygen-free solvents were employed. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and saturated $NaHCO_3$. Pentane was then dried over $MgSO_4$, stored over activated 4

(54) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525−9546.

Å molecular sieves, and distilled from potassium benzophenone ketyl under a nitrogen atmosphere. Toluene was purified by stirring with concentrated H_2SO_4, washing with saturated $NaHCO_3$, then drying over $CaCl_2$ before distillation from sodium under a nitrogen atmosphere. Spectrophotometric grade diethyl ether and reagent grade THF were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Acetonitrile was refluxed over P_2O_5 and distilled under a nitrogen atmosphere. Benzene-d_6 was vacuum distilled over sodium/potassium alloy and benzophenone.

NMR spectra were recorded in benzene-d_6 solutions on a Bruker AVB-400 instrument operating at 400.1 MHz (^{1}H), 100.7 MHz (^{13}C), and 162 MHz (^{31}P), with a Bruker AV-300 instrument operating at 300.1 MHz (^{1}H), or with a Bruker DRX-500 instrument operating at 500.1 MHz (^{1}H). Chemical shifts are reported in ppm downfield from $SiMe_4$ and were referenced internally to residual solvent resonances (^{1}H, ^{13}C) or externally to 85% H_3PO_4 (^{31}P). Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley.

All reagents were purchased from Aldrich and used as received unless stated otherwise. The 1-phenyl-2-(trimethylsilyl)acetylene was vacuum distilled and stored over 3 Å molecular sieves. Pyridine was refluxed over calcium hydride and distilled under a nitrogen atmosphere. *n*-Butyl lithium was used as a 1.6 M solution in hexanes. The zirconocene dichlorides, CpCp*$ZrCl_2$[55] and $Me_2C(\eta^5\text{-}C_5H_4)_2ZrCl_2$,[56] were prepared according to literature procedures. Compound **10** was prepared according to the method of Negishi et al.[47] Compound **11** was prepared *in situ*, and the spectroscopic characterization was consistent with the literature.[34]

CpCp*Zr[2,5-(Me$_3$Si)$_2$-3,4-Ph$_2$C$_4$] (1). To CpCp*$ZrCl_2$ (0.208 g, 0.57 mmol) in THF (15 mL), *n*-BuLi (0.7 mL, 1.1 mmol) was added dropwise via syringe at −78 °C. After stirring for 1 h at −78 °C, 1-phenyl-2-(trimethylsilyl)acetylene (0.200 g, 1.1 mmol) in THF (5 mL) was added. The reaction mixture was allowed to warm to ambient temperature over 2−3 h and was then stirred for an additional 16 h. The THF was removed under vacuum, and then pentane (20 mL) was added. The solution was cannula-filtered and pumped to dryness, and then diethyl ether (10 mL) was added until all the solid had dissolved. To this solution was slowly added acetonitrile until solid persisted in solution. The solution was cooled to −30 °C for 16 h to give the product, isolated by filtration, as yellow-orange crystals in 28% yield (0.101 g, 0.16 mmol). ^{1}H NMR: δ 6.91 (m, 6 H), 6.77 (m, 2 H), 6.71 (m, 2 H), 6.20 (s, 5 H), 1.90 (s, 15 H), −0.06 (s, 18 H). ^{13}C{^{1}H} NMR: δ 207.2 (−Zr*C*(SiMe$_3$)═CPh), 152.7 (−ZrC(SiMe$_3$)═*C*Ph), 146.2 (Ph), 131.1 (Ph), 130.7 (Ph), 126.9 (Ph), 126.5 (Ph), 125.1 (Ph), 120.2 (η^5-*C*$_5$Me$_5$), 111.3 (η^5-C$_5$H$_5$), 12.7 (η^5-C$_5$*Me*$_5$), 4.6 (−SiMe$_3$). Anal. Calcd for $C_{37}H_{48}Si_2Zr$: C, 69.42; H, 7.56. Found: C, 69.08; H, 7.50.

Me$_2$C(η^5-C$_5$H$_4$)$_2$Zr[2,5-(Me$_3$Si)$_2$-3,4-Ph$_2$C$_4$] (2). See the preparation of zirconacyclopentadiene **1** for the synthetic protocol. The amounts of reagents used were $Me_2C(\eta^5\text{-}C_5H_4)_2ZrCl_2$ (0.200 g, 0.60 mmol) in THF (10 mL), *n*-BuLi (0.75 mL, 1.2 mmol), and 1-phenyl-2-(trimethylsilyl)acetylene (0.210 g, 1.2 mmol) in THF (5 mL). Crystallization from pentane resulted in yellow crystals in 35% yield (0.130 g, 0.21 mmol). ^{1}H NMR: δ 6.87 (m, 4 H), 6.80 (m, 2 H), 6.66 (m, 4 H), 6.58 (t, 4 H, ^3J = 2.8 Hz), 5.81 (t, 4 H, ^3J = 2.8 Hz), 1.60 (s, 6 H), −0.07 (s, 18 H). ^{13}C{^{1}H} NMR: δ 198.3 (−Zr*C*(SiMe$_3$)═CPh), 145.2 (−ZrC(SiMe$_3$)═*C*Ph), 143.3 (Ph), 129.5 (Ph), 126.6 (Ph), 124.8 (Ph), 115.4 ($Me_2C(\eta^5\text{-}C_5H_4)$), 112.5 ($Me_2C(\eta^5\text{-}C_5H_4)$), 107.4 ($Me_2C(\eta^5\text{-}C_5H_4)$), 36.9 ($Me_2C(\eta^5\text{-}C_5H_4)$), 23.8 ($Me_2C(\eta^5\text{-}C_5H_4)$), 2.3 (−SiMe$_3$). Anal. Calcd for $C_{35}H_{42}Si_2Zr$: C, 68.90; H, 6.94. Found: C, 68.59; H, 6.90.

CpCp*Zr[2,3,4,5-Ph$_4$C$_4$] (3). To CpCp*$ZrCl_2$ (0.203 g, 0.56 mmol) in THF (15 mL) was added *n*-BuLi (0.7 mL, 1.1 mmol) dropwise via syringe at −78 °C. After stirring for 1 h at −78 °C, tolan (0.200 g, 1.1 mmol) in THF (5 mL) was added. The reaction mixture was allowed to warm to ambient temperature over 2−3 h and then stirred for an additional 48 h. The THF was then removed under vacuum, and then toluene (20 mL) was added. The solution was cannula-filtered and concentrated to 10 mL, and then pentane (8 mL) was added. The solution was cooled to −80 °C for 96 h to give the product, isolated by filtration, as orange crystals in 60% yield (0.216 g, 0.34 mmol). ^{1}H NMR: δ 7.00 (m, 4 H), 6.95 (m, 4 H), 6.86 (t, 4 H, ^3J = 7.8 Hz), 6.79 (m, 4 H), 6.70 (m, 4 H), 6.09 (s, 5 H), 1.79 (s, 15 H). ^{13}C{^{1}H} NMR: δ 197.5 (−Zr*C*Ph═CPh), 148.2 (−ZrCPh═*C*Ph), 144.0 (Ph), 142.9 (Ph), 131.8 (Ph), 129.1 (Ph), 127.3 (Ph), 127.1 (Ph), 124.9 (Ph), 123.4 (Ph), 121.2 (η^5-*C*$_5$Me$_5$), 112.5 (η^5-C$_5$H$_5$), 12.3 (η^5-C$_5$*Me*$_5$). Anal. Calcd for $C_{43}H_{40}Zr$: C, 79.70; H, 6.22. Found: C, 79.35; H, 6.07.

Me$_2$C(η^5-C$_5$H$_4$)$_2$Zr[2,3,4,5-Ph$_4$C$_4$] (4). See the preparation of zirconacyclopentadiene **1** for the synthetic protocol. The amounts of reagents used were $Me_2C(\eta^5\text{-}C_5H_4)_2ZrCl_2$ (0.250 g, 0.75 mmol) in THF (10 mL), *n*-BuLi (0.94 mL, 1.5 mmol), and tolan (0.402 g, 2.3 mmol) in THF (5 mL). The solid residue was purified by washing with pentane (2 × 20 mL), followed by addition of toluene (12 mL). The solution was cannula-filtered, concentrated, cooled to −30 °C for 18 h, and then cooled to −80 °C for 20 h to give the product, isolated by filtration, as orange crystals in 32% yield (0.150 g, 0.27 mmol). ^{1}H NMR: δ 7.11 (t, 4 H, ^3J = 7.6 Hz), 7.01 (m, 4 H), 6.88 − 6.79 (m, 14 H), 6.70 (m, 2 H), 5.06 (t, 4 H, ^3J = 2.8 Hz), 1.09 (s, 6 H). ^{13}C{^{1}H} NMR: δ 194.3 (−Zr*C*Ph═CPh), 149.3 (−ZrCPh═*C*Ph), 141.2 (Ph), 139.9 (Ph), 131.1 (Ph), 128.1 (Ph), 127.1 (Ph), 126.9 (Ph), 125.2 (Ph), 123.3 (Ph), 118.0 ($Me_2C(\eta^5\text{-}C_5H_4)$), 115.5 ($Me_2C(\eta^5\text{-}C_5H_4)$), 109.6 ($Me_2C(\eta^5\text{-}C_5H_4)$), 37.5 ($Me_2C(\eta^5\text{-}C_5H_4)$), 23.7 ($Me_2C(\eta^5\text{-}C_5H_4)$). Anal. Calcd for $C_{41}H_{34}Zr$: C, 79.74; H, 5.55. Found: C, 79.42; H, 5.50.

CpCp*Zr(η^2-Me$_3$SiC≡CSiMe$_3$)(pyr) (5). To CpCp*$ZrCl_2$ (0.50 g, 1.4 mmol) in THF (20 mL) was added bis(trimethylsilyl)acetylene (0.31 mL, 1.4 mmol) via syringe. This solution was cooled to −78 °C, and *n*-BuLi (1.7 mL, 2.8 mmol) was added dropwise via syringe. The mixture was stirred for 10 min at −78 °C, the cold bath was removed, and the reaction mixture was stirred for 16 h at ambient temperature. Pyridine (0.11 mL, 1.4 mmol) was then added via syringe, which caused the reaction mixture to immediately turn opaque brown. The solvent was then removed under vacuum to near dryness, pentane (30 mL) was added, and the solution was stirred for 30 min. The solution was cannula-filtered, concentrated to 10 mL, and then cooled to −80 °C for 6 days. The solvent was removed by cannula filtration, and the resulting solid was recrystallized from a concentrated pentane solution at −30 °C for 16 h to give the product, isolated by filtration, as dark purple crystals in 16% yield (0.122 g, 0.23 mmol). ^{1}H NMR: δ 8.34 (m, 2 H), 6.87 (m, 1 H), 6.55 (m, 2 H), 5.70 (s, 5 H), 1.58 (s, 15 H), 0.33 (s, 18 H). ^{13}C{^{1}H} NMR: δ 222.8 (−Zr*C*(SiMe$_3$)═*C*(SiMe$_3$), detected by gHMBC experiment), 153.4 (pyr), 136.1 (pyr), 123.1 (pyr), 115.0 (η^5-*C*$_5$Me$_5$), 108.5 (η^5-C$_5$H$_5$), 11.9 (η^5-C$_5$*Me*$_5$), 3.4 (−SiMe$_3$). Anal. Calcd for $C_{28}H_{43}NSi_2Zr$: C, 62.16; H, 8.01; N, 2.59. Found: C, 62.37; H, 8.10; N, 2.72.

Me$_2$C(η^5-C$_5$H$_4$)$_2$Zr(η^2-Me$_3$SiC≡CSiMe$_3$)(pyr) (6). A Schlenk tube was loaded with $Me_2C(\eta^5\text{-}C_5H_4)_2ZrCl_2$ (0.250 g, 0.75 mmol), magnesium powder (0.091 g, 3.75 mmol), and mercury chloride (0.204 g, 0.75 mmol) and was then cooled to −78 °C. A solution of bis-(trimethylsilyl)acetylene (0.17 mL, 0.75 mmol) in THF (10 mL) was added, and the mixture was then stirred for 1.5 h while warming to −20 °C. The flask was then placed in an ice bath for 15 min, and pyridine (0.06 mL, 0.75 mmol) was added via syringe. The reaction mixture was allowed to warm to ambient temperature and was stirred for 16 h. The solvent was removed under vacuum, then pentane (20 mL) was added, and the solution was stirred for 15 min. The solution was cannula-filtered, concentrated to 5 mL, and cooled to −30 °C for 18 h to give the product, isolated by filtration, as dark purple crystals in 46% yield (0.176 g, 0.34 mmol). ^{1}H NMR: δ 8.64 (m, 2 H), 6.80 (m, 1 H), 6.38 (m, 2 H), 6.13 (m, 2 H), 5.34 (m, 4 H), 4.93 (m, 2 H),

(55) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793−799.
(56) Quijada, R.; Dupont, J.; Silveira, D. C.; Miranda, M. S. L.; Scipioni, R. B. *Macromol. Rapid Commun.* **1995**, *16*, 357−362.

1.55 (s, 3 H), 1.42 (s, 3 H), 0.55 (s, 9 H), 0.05 (s, 9 H). $^{13}C\{^1H\}$ NMR: δ 217.6 ($-ZrC(SiMe_3)$=$C(SiMe_3)$), 195.7 ($-ZrC(SiMe_3)$=$C(SiMe_3)$), 152.8 (pyr), 136.5 (pyr), 123.0 (pyr), 122.9 ($Me_2C(\eta^5$-$C_5H_4)$), 113.9 ($Me_2C(\eta^5$-$C_5H_4)$), 108.9 ($Me_2C(\eta^5$-$C_5H_4)$), 94.9 ($Me_2C(\eta^5$-$C_5H_4)$), 92.1 ($Me_2C(\eta^5$-$C_5H_4)$), 35.7 ($Me_2C(\eta^5$-$C_5H_4)$), 24.7 ($Me_2C(\eta^5$-$C_5H_4)$), 24.3 ($Me_2C(\eta^5$-$C_5H_4)$), 2.5 ($-SiMe_3$), 2.3 ($-SiMe_3$). Anal. Calcd for $C_{26}H_{37}NSi_2Zr$: C, 61.11; H, 7.30; N, 2.74. Found: C, 60.88; H, 7.35; N, 2.59.

CpCp*Zr(η^2-Me$_3$SiC≡CPh)(PMe$_3$) (7). See the preparation of zirconacyclopropene **6** for synthetic protocol. The amounts of reagents used were $Cp^*CpZrCl_2$ (0.40 g, 1.1 mmol), magnesium powder (0.13 g, 5.5 mmol), mercury chloride (0.30 g, 1.1 mmol), 1-phenyl-2-(trimethylsilyl)acetylene (0.19 g, 1.1 mmol), and PMe_3 (0.11 mL, 1.1 mmol) in THF (15 mL). Crystallization from pentane resulted in yellow crystals in 51% yield (0.305 g, 0.56 mmol). ^1H NMR: δ 7.20 (t, 2 H, $^3J = 8.5$ Hz), 6.94 (m, 1 H), 6.80 (m, 2 H), 5.40 (s, 5 H), 1.74 (s, 15 H), 0.83 (d, 9 H, $^2J_{H-P} = 5$ Hz), 0.37 (s, 9 H). $^{31}P\{^1H\}$ NMR: δ −10.2. Anal. Calcd for $C_{29}H_{43}PSiZr$: C, 64.27; H, 8.00. Found: C, 64.27; H, 8.20.

Me$_2$C(η^5-C$_5$H$_4$)$_2$Zr(η^2-Me$_3$SiC≡CPh)(PMe$_3$) (8). See the preparation of zirconacyclopropene **6** for synthetic protocol. A change to the above procedure was that the reaction mixture was stirred for only 2 h at ambient temperature before removal of THF. The amounts of reagents used were $Me_2C(\eta^5$-$C_5H_4)_2ZrCl_2$ (0.322 g, 0.97 mmol), magnesium powder (0.118 g, 4.85 mmol), mercury chloride (0.263 g, 0.97 mmol), 1-phenyl-2-(trimethylsilyl)acetylene (0.19 mL, 0.97 mmol), and PMe_3 (0.1 mL, 1 mmol) in THF (10 mL). Crystallization from pentane resulted in yellow crystals in 29% yield (0.145 g, 0.28 mmol). ^1H NMR: δ 7.20 (t, 2 H, $^3J = 8$ Hz), 6.96 (m, 1 H), 6.72 (m, 2 H), 6.43 (m, 2 H), 5.09 (m, 2 H), 4.97 (m, 2 H), 4.92 (m, 2 H), 1.64 (s, 3 H), 1.38 (s, 3 H), 0.81 (d, 9 H, $^2J_{H-P} = 6$ Hz), 0.35 (s, 9 H). $^{31}P\{^1H\}$ NMR: δ −7.1. Anal. Calcd for $C_{27}H_{37}SiPZr$: C, 63.35; H, 7.29. Found: C, 63.38; H, 7.29.

Cp$_2$Zr[2,5-(Me$_3$Si)$_2$-3,4-Ph$_2$C$_4$] (9). See the preparation of zirconacyclopentadiene **1** for the synthetic protocol. The amounts of reagents used were Cp_2ZrCl_2 (0.20 g, 0.68 mmol) in THF (15 mL), *n*-BuLi (0.85 mL, 1.4 mmol), and 1-phenyl-2-(trimethylsilyl)acetylene (0.24 g, 1.4 mmol) in THF (5 mL). Crystallization from pentane resulted in yellow crystals in 26% yield (0.100 g, 0.18 mmol). ^1H NMR: δ 6.88 (t, 4 H, $^3J = 7.3$ Hz), 6.77 (t, 2 H, $^3J = 7.5$ Hz), 6.68 (d, 4 H, $^3J = 7.3$ Hz), 6.16 (s, 10 H), −0.16 (s, 18 H). This is consistent with the reported ^1H NMR spectrum.[57]

Reaction of Cp$_2$Zr[2,5-(Me$_3$Si)$_2$-3,4-Ph$_2$C$_4$] (9) with Tolan. Zirconacycle **9** (ca. 6.5 mg, 11 μmol), tolan (ca. 21 mg, 118 μmol), and ferrocene (ca. 5 mg, 27 μmol) were loaded into a Teflon-sealed NMR tube and then dissolved in benzene-d_6 (ca. 500 mg). The tube was then heated at 50 °C directly in the spectrometer for 1 h.

Data points were gathered by ^1H NMR spectroscopy, and the rate of disappearance of **9** was monitored by integrating the $-SiMe_3$ peak relative to that of Cp_2Fe. Rate constants were calculated from first-order plots using data from the first three to five half-lives, and the observed rate constant ($k_{obs} = 0.88(3) \times 10^{-3}$ s^{-1}) is an average of three runs.

Kinetic Study of the Zirconacylopentadiene Fragmentation with PMe$_3$. Zirconacyclopentadienes **1**, **2**, or **9** (ca. 9.7 μmol) and ferrocene (ca. 2 mg, 10.7 μmol) were dissolved in benzene-d_6 (ca. 500 mg) and then loaded into a Teflon-sealed NMR tube. To this solution was added PMe_3 (10 μL, 97 μmol), and the samples containing **1** were quickly frozen to prevent fragmentation before analysis.

Data points were gathered by ^1H NMR spectroscopy, and the rate of disappearance of **1**, **2**, or **9** was monitored by integrating the $-SiMe_3$ peak relative to that of Cp_2Fe. Rate constants were calculated from first-order plots using data from the first three to five half-lives. All high-temperature analyses were performed directly in the spectrometer, and the temperature was calibrated with an external ethylene glycol standard.[58]

Influence of [PMe$_3$] on the Rate of Zirconacyclopentadiene Fragmentation. Zirconacyclopentadienes **1**, **2**, or **9** (ca. 6 μmol) and ferrocene (ca. 2 mg, 10.7 μmol) were dissolved in benzene-d_6 (ca. 500 mg) and then loaded into a Teflon-sealed NMR tube. To this solution was added PMe_3 in varying concentrations (three different concentrations for each), and the samples containing **1** were quickly frozen to prevent fragmentation before analysis. Experiments for zirconacyclopentadiene **1** were performed at 20 °C, those for **2** were done at 75 °C, and those for **9** were done at 50 °C.

Data points were gathered by ^1H NMR spectroscopy, and the rate of disappearance of **1**, **2**, or **9** was monitored by integrating the $-SiMe_3$ peak relative to that of Cp_2Fe. Rate constants were calculated from first-order plots using data from the first three to five half-lives. See the Supporting Information for further details.

Supporting Information Available: Tables of bond lengths and angles, details of the kinetic experiments, and the X-ray crystallographic data for compounds **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA800025U

(57) Erker, G.; Zwettler, R.; Kruger, C.; Schlund, R.; Hylakryspin, I.; Gleiter, R. *J. Organomet. Chem.* **1988**, *346*, C15−C18.

(58) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319−321.