Monocyclopentadienyltitanium Aryloxide Complexes: Preparation, Characterization, and Application in Cyclization Reactions

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A variety of monocyclopentadienyltitanium aryloxide complexes were prepared, characterized by X-ray crystallography, and used to catalyze or mediate cyclization reactions. Structural characterization allowed for the comparison of steric parameters of various 2,6-disubstituted aryloxide ligands. Transformations of dienes and enynes—including the catalysis of a 1,6-diene cycloisomerization and the intramolecular Pauson−Khand reaction—were investigated. A titanium metallacycle was prepared from a sterically hindered enyne containing a trisubstituted olefin. The Pauson−Khand reaction of trimethylsilyl-substituted enynes was promoted to generate α-silylcyclopentenones.

Introduction

Reactions that form new carbon−carbon bonds from unsaturated compounds such as alkynes and olefins have advanced dramatically by the application of low-valent group 4 metal complexes. Examples include reactions promoted by titanium or zirconium metallocenes (Cp_2ML_n)[1] or titanium−alkoxide complexes ($(RO)_2TiL_n$, typically R = *i*-Pr).[2−5] Titanium−aryloxide complexes mediate the formation of carbon−carbon bonds from unsaturated functionality, and investigations have typically focused on ligation with 2,6-disubstituted aryloxides.[6] Recent examples of titanium−aryloxide catalysts for organic transformations have also emerged.[7,8] Furthermore, monocyclopentadienyl complexes[9−11] catalyze the polymerization of olefins and a variety of organic transformations.[12] The catalysts are particularly noted for the open nature of their active sites, which allows for incorporation of α-olefins such as styrene into polymers.[9]

We have been interested in the application of titanium metallocene complexes to carbocyclization reactions, particularly the intramolecular Pauson−Khand reaction (eq 1).[13−16] Titanocene dicarbonyl ($Cp_2Ti(CO)_2$) can serve as a cyclocarbonylation catalyst for a variety of 1,6- and

(1) For reviews of cyclization reactions mediated or catalyzed by titanocene and zirconocene complexes, see: (a) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723−742. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058. (c) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696−1701. (d) Negishi, E.-i.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124−130. (e) Ohff, A.; Pulst, S.; Lefeber, C.; Peulecke, N.; Arndt, P.; Burkalov, V. V.; Rosenthal, U. *Synlett* **1996**, 111−118. (f) Negishi, E.-i.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755−769.

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(3) For intramolecular cyclization reactions mediated by $(i\text{-PrO})_2TiL_n$, see: (a) Urabe, H.; Hata, T.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 4261−4264. (b) Urabe, H.; Takeda, T.; Sato, F. *Tetrahedron Lett.* **1996**, *37*, 1253−1256. (c) Urabe, H.; Sato, F. *J. Org. Chem.* **1996**, *61*, 6156−6157. (d) Suzuki, K.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **1996**, *118*, 8729−8730. (e) Urabe, H.; Suzuki, K.; Sato, F. *J. Am. Chem. Soc.* **1997**, *119*, 10014−10027. (f) Urabe, H.; Takeda, T.; Hideura, D.; Sato, F. *J. Am. Chem. Soc.* **1997**, *119*, 11295−11305. (g) Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 1245−1255.

(4) For recent and lead references of carbon−carbon bond forming reactions mediated by $(i\text{-PrO})_2TiL_n$, see: (a) Corey, E. J.; Rao, S. A.; Noe, M. C. *J. Am. Chem. Soc.* **1994**, *116*, 9345−9346. (b) Lee, J.; Kim, H.; Cha, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 4198−4199. (c) Hideura, D.; Urabe, H.; Sato, F. *Chem. Commun.* **1998**, 271−272. (d) Williams, C. M.; Chaplinski, V.; Schreiner, P. R.; de Meijere, A. *Tetrahedron Lett.* **1998**, *39*, 7695−7698. (e) Hamada, T.; Suzuki, D.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 7342−7344.

(5) For reviews of reactions mediated by $(i\text{-PrO})_2TiL_n$, see: (a) Sato, F.; Urabe, H.; Okamoto, S. *Synlett* **2000**, 753−775. (b) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835−2886.

(6) For recent and lead references, see: (a) Hill, J. E., Balaich, G., Fanwick, P. E., Rothwell, I. P. *Organometallics* **1993**, *12*, 2911−2924. (b) Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, W. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 8630−8641. (c) Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1999**, *18*, 4442−4447.

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(8) Okamoto, S.; Livinghouse, T. *J. Am. Chem. Soc.* **2000**, *122*, 1223−1224.

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(10) (a) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649−1651. (b) Amor, F.; Okuda, J. *J. Organomet. Chem.* **1996**, *520*, 245−248. (c) Okuda, J.; Eberle, T.; Spaniol, T. P. *Chem. Ber.* **1997**, *130*, 209−215.

(11) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640.

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(13) (a) Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 4912−4913. (b) Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8593−8601.

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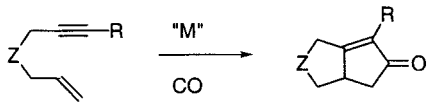
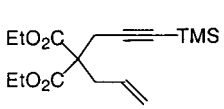
1,7-enynes and demonstrates excellent functional group tolerance, particularly for an early-metal complex.[15] A

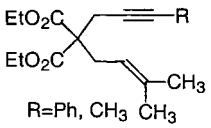


(1)

limitation of this method, however, is the reluctance of the relatively bulky titanocene fragment to react with sterically hindered alkynes or olefins. For example, we have found that enynes such as **1** and **2** are not cyclocarbonylated by $Cp_2Ti(CO)_2$.



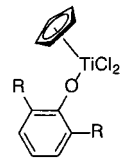
1

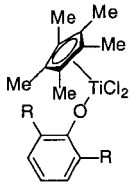


2

Presented with the steric limitations of a titanocene-based system and the volume of current literature describing early-metal catalysts that have evolved beyond a traditional metallocene framework,[9,17] we felt that more reactive catalysts for the Pauson−Khand reaction might be prepared by exploring new ligand frameworks. We sought a ligand set that would exhibit reactivity analogous to titanocene complexes while providing a less crowded coordination environment. Considering the use of titanium−alkoxide and −aryloxide[6] complexes for cyclization reactions[3,7,8] and the open nature of monocyclopentadienyl catalysts,[9] we chose to replace a cyclopentadienyl ligand of the titanocene fragment with an aryloxide. Monocyclopentadienyltitanium aryloxide complexes can be readily prepared from the corresponding cyclopentadienyltitanium trichloride and an appropriate phenol.[18] Phenols bearing substituents that provide a wide range of steric and electronic properties are commercially available or can be easily prepared, allowing for fine-tuning of the aryloxide complexes' reactivity.

The first examples of mixed monocyclopentadienyltitanium aryloxide complexes were reported by Whitby, who investigated their electrochemistry.[18] Pure products with 2,6-substituted-aryloxide ligands could be cleanly isolated. These were prepared by two methods: reaction of $CpTiCl_3$ with the appropriate phenol and Et_3N in Et_2O at room temperature or reaction of the corresponding sodium phenolate with $CpTiCl_3$ in toluene at 100 °C. More recently, researchers at Sumitomo Chemical Company have reported the preparation of monocyclopentadienyltitanium aryloxide complexes by reaction of $CpTiCl_3$ or Cp^*TiCl_3 (pentamethylcyclopentadienyltitanium trichloride) with various lithium phenoxides in Et_2O, toluene, or CH_2Cl_2.[19] This study provided





$Cp(DPP)TiCl_2$	**3a**	R = Ph	$Cp^*(DPP)TiCl_2$	**4a**	R = Ph
$Cp(DIPP)TiCl_2$	**3b**	R = *i*-Pr	$Cp^*(DIPP)TiCl_2$	**4b**	R = *i*-Pr
$Cp(DME)TiCl_2$	**3c**	R = OMe			
$Cp(DM)TiCl_2$	**3d**	R = Me			

Figure 1. Monocyclopentadienyltitanium aryloxide complexes.

structural characterization of 2,6-diisopropylphenoxide derivatives and demonstrated that complexes of this type exhibit catalytic activity for alkene polymerization (with appropriate activators such as MAO).

Results and Discussion

Synthesis and Characterization of Monocyclopentadienyltitanium Aryloxide Complexes. We have investigated the chemistry of the group of monocyclopentadienyltitanium aryloxide complexes shown in Figure 1. Dichlorides **3b** and **3d** were prepared as described by Whitby.[18] As anticipated, complex **3a**, bearing sterically demanding 2,6-diphenyl substitution, was easily prepared by the same method, using 2,6-diphenylphenol and triethylamine.

We were interested in including the 2,6-dimethoxyphenolate ligand (complex **3c**) in this study because of the potential for chelation of the ortho methoxy substituents. This compound, however, could not be prepared by the reported procedures. We found that use of the corresponding potassium phenoxide in toluene at room temperature provided for clean conversion to the desired complex. The pentamethylcyclopentadienyl analogue of **3a** (**4a**) was prepared from Cp^*TiCl_3 and the corresponding sodium phenolate. The pentamethylcyclopentadienyl complex **4b**[19] was not prepared or investigated in this study, but its X-ray crystal data are included for structural comparison (Table 1).

The titanium dichlorides were isolated as highly colored crystalline materials that were yellow, orange, and red. Variation of substituents on the aryloxide ligands allowed great flexibility for both steric and electronic perturbations relative to a cyclopentadienyl ligand. To provide an indication of how these parameters are affected in the mixed complexes, they were structurally characterized by X-ray crystallography. Representations of the crystal structures we have obtained are shown in Figures 2−4.

The calculation of cone angles provides a means to compare steric paramaters for a variety of ligands.[20] For reference, Tolman has estimated the symmetric cone angle of a cyclopentadienyl ligand to be 136°.[20] In the case of aryloxide ligands, however, Wolczanski has put forth a more appropriate spatial perception of this type of ligand as a "wedge" since it does not fill a true conical region.[21] This spatial representation is analogous to a model used to describe nucleophilic carbene ligands,

(15) (a) Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 9450−9451. (b) Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 5881−5898.

(16) (a) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688−11689. (b) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 7026−7033.

(17) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

(18) Fussing, I. M. M.; Pletcher, D.; Whitby, R. J. *J. Organomet. Chem.* **1994**, *470*, 109−117.

(19) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152−2154.

(20) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(21) Wolczanski, P. T. *Polyhedron* **1995**, *14*, 3335−3362.

Table 1. Selected Bond Angles (deg) and Bond Lengths (Å)

	3a[a]	**3b**	**3c**	**4a**	**4b**
R	Ph	*i*-Pr	OMe	Ph	*i*-Pr
			Bond Lengths		
Ti−O	1.7900(18)	1.760(4)	1.7781(18)	1.811(3)	1.772(3)
Ti−Cl(1)	2.2522(10)	2.262(1)	2.2710(10)	2.2693(13)	2.305(2)
Ti−Cl(2)	2.2542(11)	2.262(1)	2.2680(1)	2.2865(14)	2.305(2)
Ti−Cp	2.0117(4)	1.99	2.0420(3)	2.0310(4)	2.03
			Angles		
C−O−Ti	151.17(7)	163.0(4)	161.37(17)	160.6(3)	173.0(3)
Cl(1)−Ti−Cl(2)	101.23(5)	104.23(7)	102.24(3)	98.70(5)	103.45(5)
A_L	157	123	122	148	121
A_h	59	94	37	53	92

[a] Values are the average of those for the four nearly identical structures in the asymmetric unit.

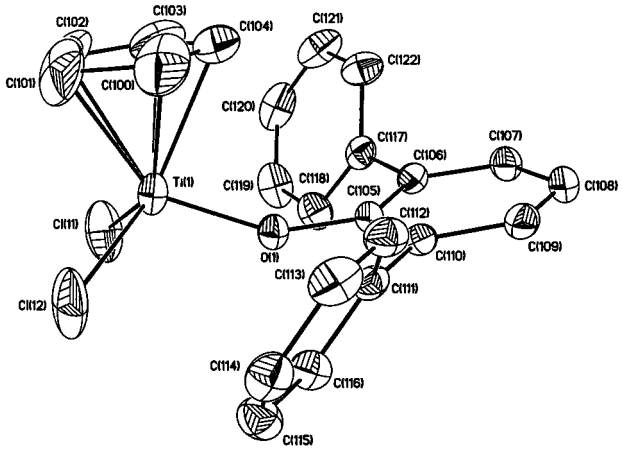


Figure 2. ORTEP plot of the solid-state molecular structure of **3a**. Thermal ellipsoids are shown at the 30% probablility level.

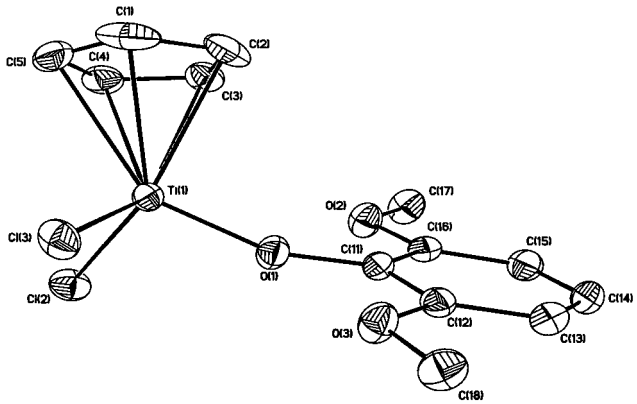


Figure 3. ORTEP plot of the solid-state molecular structure of **3c**. Thermal ellipsoids are shown at the 30% probablility level.

imidazol-2-ylidenes.[22,23] The steric environment of the wedge can therefore be described by two parameters, Spatial perceptions the angles A_L and A_H (Figure 5).[24]

Steric parameters for a wedge that describes each of the aryloxide ligands of interest in this study were calculated from the bond lengths and angles obtained from structural data. To do so, a van der Waals radius of 1.08 Å was assumed for each of the hydrogen atoms from which distances were measured.[25] Because single

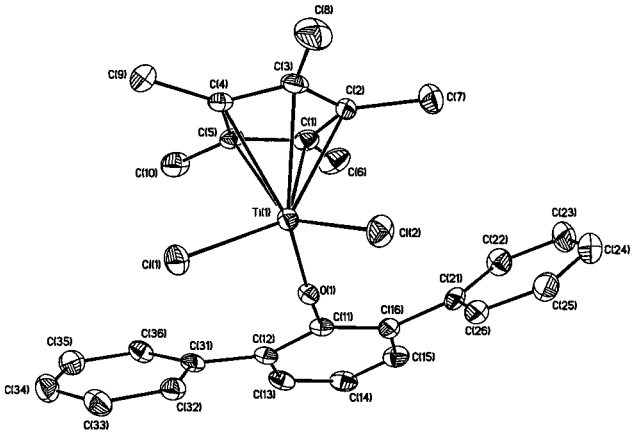


Figure 4. ORTEP plot of the solid-state molecular structure of **4a**. Thermal ellipsoids are shown at the 30% probablility level.

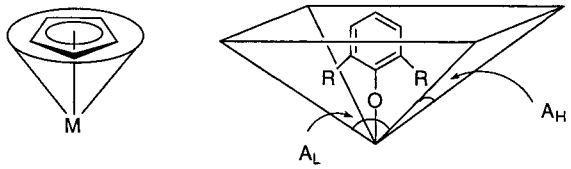


Figure 5. Spatial perceptions of the conical displacement of a cyclopentadienyl ligand and the wedge describing an aryloxide ligand.

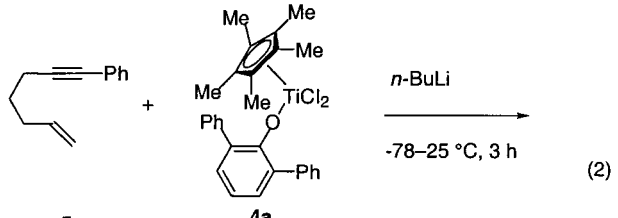
crystals were not obtained for the dimethyl complex **3d**, values (A_L = 101°; A_H = 59°) were obtained by computationally superimposing the methyl substituents onto the ligand framework of the DIPP complex **3b**. Comparisons of the steric parameters derived from each ligand (Table 1) reveal the distinct packing geometry attained by each aryloxide. The most isotropic of the aryloxides is the diisopropylphenoxide (DIPP) ligand (**3b**, **4b**), and the most anisotropic is the diphenylphenoxide (DPP) ligand (**3a**, **4a**), which is almost three times as "long" (A_L) as it is "high" (A_H). The presence of a Cp vs Cp* does not appear to significantly affect the steric constraints of the aryloxide ligand.

While it is difficult to quantify the number of electrons donated from an aryloxide ligand, structural information is often used as an estimate. Rothwell's work with aryloxide complexes, however, demonstrates little correlation based on this approach.[26] For example, the angle of the M−O−C linkage along with the M−O bond length could be considered indicative of the aryloxide−

(22) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913−921.
(23) Herrmann, W. A.; Kocher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162−2187.
(24) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *617*, 17−27.
(25) Srinivasan, R.; Hariharan, M.; Vijayalakshmi, J. *Curr. Sci.* **1987**, *56*, 942−945.

metal bond order.[21] Thus, as the M−O−C linkage approaches linearity, a significant involvement of both p orbitals may be inferred. Likewise, a shortening of the M−O bond would reflect higher bond strength. Given that the Cp* is more electron donating than Cp, by electronic arguments alone, one would predict that the pentamethylcyclopentadienyl-ligated complexes would attain less π-donation from the aryloxide, thus contracting the Ti−O−C bond angle. However, in moving from the Cp to Cp* complexes, the Ti−O−C angle in fact increases by 10° on average. The C−O bond distance is either lengthened slightly or remains unchanged. Our data therefore reinforce Rothwell's warning against the estimation of π-donation in niobium− and tantalum−aryloxide complexes from bond angles.[26] The expanded Ti−O−C bond angle in the Cp* complexes is consistent with the sterically demanding size of the Cp* ligand that can "push" the aryloxide ligand away toward linearity (in the Cp analogues, the aryloxide ligand is tilted upward toward the Cp).

Cyclization Studies. The monocyclopentadienyltitanium aryloxide complexes were activated by reduction of the Ti(IV) dichlorides with Grignard reagents or *n*-BuLi at low temperature (−78 °C) to yield the formally Ti(II)−olefin complexes. A resulting color change of the solution from bright orange to deep brown was observed. Metallacycles were generated when the monocyclopentadienyl complex **3b** (eq 3), but not the pentamethylmonocyclopentadienyl complex **4a** (eq 2), was



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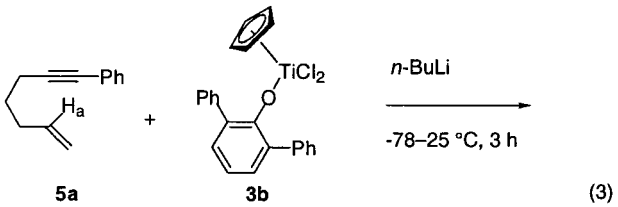

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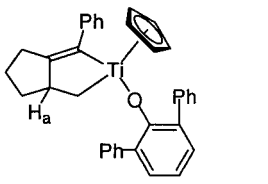


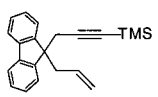
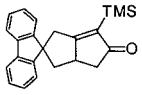
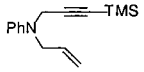
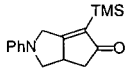
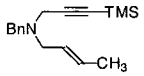
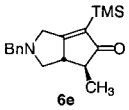
7

H_a ^{1}H NMR δ 2.97 (m, 1 H)

Cp ^{1}H NMR δ 5.53 (s, 5 H)

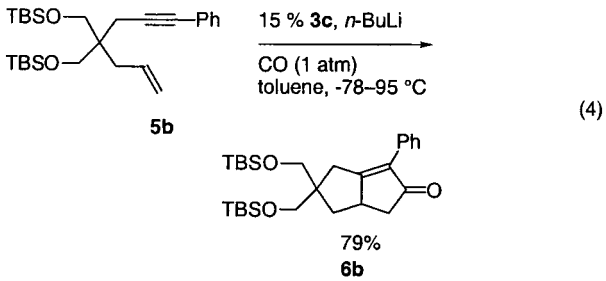
reduced in the presence of an enyne. Formation of metallacycle **7** was evidenced by the distinct change in the ^{1}H NMR resonance for the olefinic proton, H_a, from δ 5.65 to δ 2.97. Preliminary experiments also demonstrated that such complexes were susceptible to carbonylation. The monocyclopentadienyl complexes (**3a**−**d**) were therefore investigated as catalysts for the Pauson−Khand reaction.

Table 2. "Cp(DPP)Ti"-Mediated Cyclocarbonylation of Trimethylsilyl-Substituted Enynes

enyne	cyclopentenone	equiv Ti	P_{CO}(atm)	yield[a]
 **5c**	 **6c**	1	0.3	66%[b], 56%
		0.30	2.1	48%[b]
 **5d**	 **6d**	0.30	2.1	38%
 **5e**	 **6e**	0.30	2.1	81%[c]

[a] Unless otherwise indicated, yield is for isolated product of >95% purity for an average for two or more runs. [b] Yield determined by GC using an internal standard. [c] Yield represents the combined average isolated yields of 66% and 15% for the *trans*-(isomer shown) and *cis*-cyclopentenone isomers, respectively. The crude reaction mixture is a 3:1 ratio of isomers.

The monocyclopentadienyltitanium aryloxide complex **3c** served as an efficient catalyst for the cyclocarbonylation of enyne **5b** (eq 4). In the example shown in eq 4,



(4)

the optimal catalyst was generated by reduction of Cp(DME)$TiCl_2$ **3c** by *n*-BuLi in toluene.[27,28] The highest yields of cyclopentenone product **6b** were realized when the reaction was carried out under 1 atm of CO at 95 °C. The cyclization of more sterically hindered substrates, however, benefited from the use of 2.1 atm of CO (Table 2).

The monocyclopentadienyltitanium aryloxide complexes exhibit reactivity comparable to titanocene complexes but are somewhat less tolerant of certain functional groups. For example, simple enynes containing a malonic acid diester group as part of the alkyne−olefin linker are excellent substrates for titanocene-catalyzed reactions.[15] These compounds were not suitable sub-

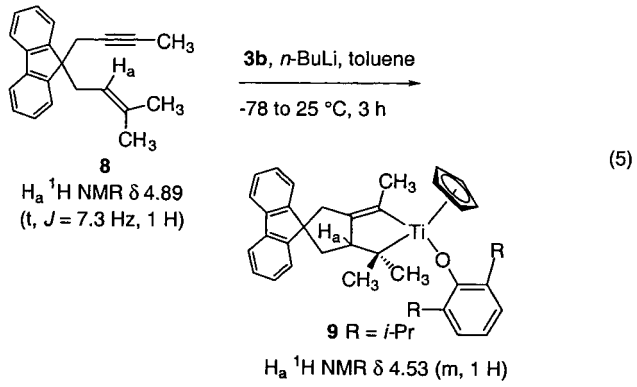
(26) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963−968.

(27) Negishi, E.-i.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, S. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336−3346.

(28) Hicks, F. A.; Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 2713−2718.

strates for reactions with monocyclopentadienyltitanium aryloxide complexes and produced complex product mixtures.[29]

The monocyclopentadienyltitanium aryloxide complexes (**3**) were further investigated for their performance in cyclization reactions of sterically hindered substrates for which titanocene complexes failed. When **3b** was reduced in the presence of an enyne bearing a trisubstituted olefin such as **8**, the corresponding metallacycle **9** was indeed formed (eq 5). This substrate did not form a metallacycle under similar conditions with titanocene complexes.



(5)

Identification of complex **9** was challenging due to an unusually low-field ^{1}H NMR shift of δ 4.53 for H_a and our inability to isolate single crystals despite the presence of the fluorenyl moiety. The metallacycle structure was assigned in part based on characteristic ^{13}C NMR shifts in the metallacyclopentene ring (Figure 6), particularly the olefinic carbon bound to the Ti at δ 201.2. In an analogous biscyclopentadienyl-ligated metallacycle, for which a crystal structure was obtained, the corresponding carbon resonance appears at δ 187.8.[30] In titanocene−alkyne complexes, the corresponding resonances are typically in the range of δ 106−135.[31] The other three carbon resonances of the metallacyclic portion of **9** (δ 144.5, 38.9, 72.4) also correlate closely with the corresponding resonances of a known biscyclopentadienylmetallacycle (δ 151.54, 39.80, 70.6).[30] Furthermore, an HMBC[32] NMR experiment indicates a cyclized structure; the most compelling HMBC data were cross-peaks from H_a to C_b and C_c (Figure 6). A combination of these experiments with HMQC[32] and COSY[32] data allowed for the assignment of ^{13}C and ^{1}H

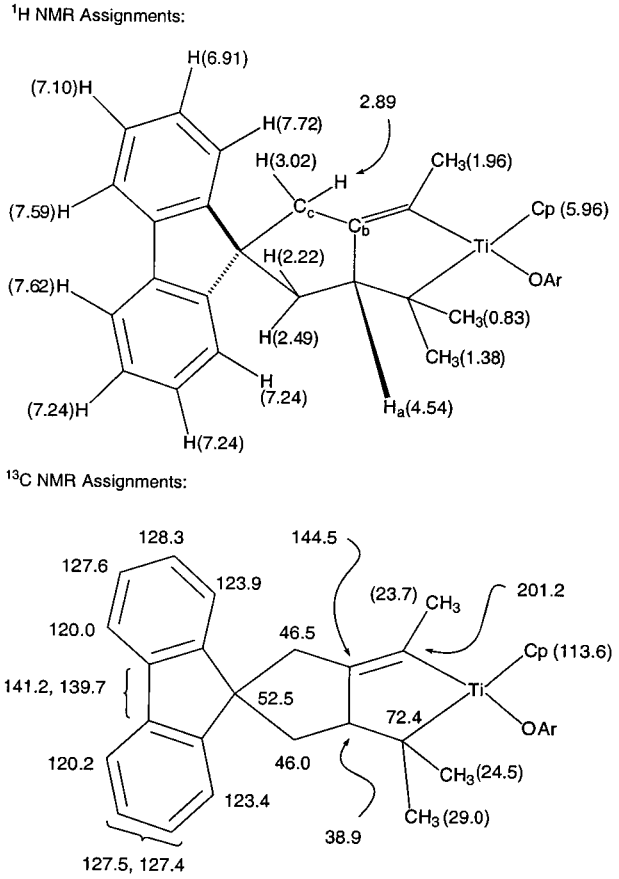
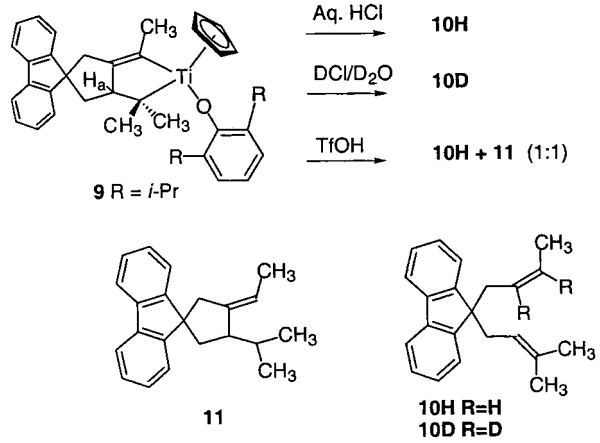


Figure 6. ^{1}H and ^{13}C assignments for metallacycle **9**.

Scheme 1. Quenching of Metallacycle 9



resonances for compound **9** as shown in Figure 6. A possible explanation for the unusual ^{1}H NMR shift of H_a is in close proximity to one of the arene rings of the flourenyl group, as evidenced by NOE correlations.

Protonolysis or deuteriolysis of metallacycle **9** with aqueous acid (HCl or DCl) resulted in acyclic products **10H** and **10D**, indicating that under these conditions retrocyclization occurs faster than protonation of the Ti−C bond (Scheme 1). Quenching of the metallacycle with anhydrous HCl (at either −78 or 25 °C) afforded the cyclic product **11**, but it was contaminated with the acyclic product **10H** along with compounds resulting from the addition of HCl to the trisubstituted double bonds. Reaction of **9** with triflic acid cleanly furnished a 1:1 mixture of the cyclic and acyclic products **10H** and

(29) Side reactions are probably a result of the experimental procedure used: The dichloride complexes are reduced with *n*-BuLi in the presence of the substrate. Addition of *n*-BuLi to the ester group may compete with reduction of the dichloride. Catalyst activation in the absence of a substrate also leads to diminished yields, however, because binding of the substrate may inhibit decomposition pathways for the putative Ti(II) species.

(30) Eriksson, M.; and Buchwald, S. L. Unpublished results. The structure of the biscyclopentadienyl-ligated metallacycle is shown below; ^{13}C NMR data were obtained in C_6D_6.

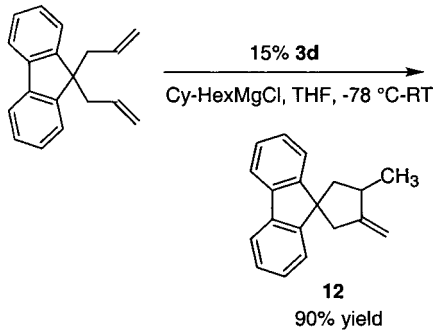
(31) Rosenthal, U.; Oehme, G.; Burlakov, V. V.; Petrovskii, P. V.; Shur, V. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *391*, 119−122.

(32) The HMQC (heteronuclear multiple quantum coherence) experiment correlates proton and carbon nuclei via ^1J(C,H). A cross-peak is observed between a carbon and attached protons. In the HMBC (heteronuclear multible bond correlation) experiment, longer range correlations via ^2J(C,H) and ^3J(C,H) are observed while ^1J(C,H) are suppressed. The commonly used homonuclear experiment, COSY (correlation spectroscopy), indicates ^{1}H−^{1}H spin-coupling cross-peaks. For guidelines and lead references see: Braun, S.; Kalinowski, H.-O.; Berger, S. *150 and More Basic NMR Experiments, A Practical Course*; Wiley-VCH: Weinheim, 1998; Chapter 10.

11. To the best of our knowledge, metallacycle **9** is the first example of an α,α-disubstituted titanacylopentene that has been prepared from a trisubstituted olefin.[33] Furthermore, such a hindered complex was not formed from biscyclopentadienyltitanium complexes under similar conditions.

The cyclocarbonylation of trimethylsilyl-substituted enynes generates α-silylcyclopentenones, which can be useful synthetic intermediates. The cyclized products can be protodesilylated to provide unsubstituted cyclopentenones[34] or converted to α-bromo- or α-iodocyclopentenones.[27,35] These are potential substrates for a wide range of reactions.[36] Although trimethylsilyl-substituted enynes can be cyclized with stoichiometric amounts of zirconocene or (η^2-olefin)Ti(O-*i*-Pr)$_2$ complexes, such substrates are unreactive toward cyclization in the presence of titanocene complexes.[13] We have found, however, that replacement of a cyclopentadienyl with an appropriate aryloxide ligand allows for the cyclocarbonylation of trimethylsilyl-substituted enynes. Table 2 illustrates several examples of the cyclocarbonylation of trimethylsilyl-substituted enynes using the DPP complex **3a**. A variety of conditions were screened and, although substoichiometric amounts of the metal complex can be used for this reaction, efficient catalysis was not realized. The disubstituted olefin **5e** was cyclocarbonylated in good yield with minor amounts of the *trans*-cyclopentenone product being formed. Both *trans*- and *cis*-cyclopentenone isomers were easily separated by chromatography, and each was isolated in 66% and 15% yield, respectively.

Catalysts for the cycloisomerization of dienes are of interest due to the versatility of the cyclized products as well as the ready availability of substrates.[8,37] When **3d** was reduced in the presence of a 1,6-diene, the corresponding *exo*-olefinic cyclopentane product **12** could be isolated in excellent yield (90%, eq 6). This protocol was superior to those attempted using *n*-BuLi/toluene



12
90% yield

(6)

and warming to room temperature (24% conversion) or 95 °C (91% conversion to a mixture of isomers). Complex **3d** was a more effective precatalyst than the sterically demanding DIPP (**3a**) or DPP (**3b**) complexes, which gave rise to only small amounts (5% was detected by GC analysis) of the cyclized product. Introduction of CO (16 psig) into the reaction mixture inhibited cyclization such that diminished amounts of **12** were formed (23% was detected by GC analysis), but no products of carbonylative processes were observed. Attempts to use $CpTiCl_3$ as a catalyst precursor under the optimized reaction conditions resulted in no cyclized product.

Summary and Conclusions

We have prepared several monocyclopentadienyltitanium aryloxide complexes and investigated their application in carbon−carbon bond forming reactions including cyclizations of enynes and dienes. The titanium dichloride species were characterized by X-ray crystallography, which allowed for the comparison of steric parameters for each of the differently substituted aryloxide ligands.

Of particular interest to our research was the application of these complexes to the cyclocarbonylation of enynes, specifically to sterically challenging enynes that were unreactive with titanocene systems. Reduction of the dichloride complexes in the presence of enynes provided corresponding metallacycles, which were susceptible to protonolysis and CO insertion. Furthermore, monocyclopentadienyltitanium aryloxide complexes served as precatalysts for the cyclocarbonylation of enynes. Substitution of an aryloxide ligand for a cyclopentadienyl ligand allowed for the preparation of titanacyclopentenes derived from trisubstituted olefins and of α-trimethylsilylcyclopentenones, compounds that could not be accessed using titanocene complexes.

The efficiency of the carbonylation and cyclization reactions were dependent upon the substitution of the aryloxide ligand. Metallacycles derived from trisubstituted olefins were obtained most efficiently from the diisopropyl complex **3b**. Phenyl-substituted enynes were catalytically cyclocarbonylated using the dimethoxy complex **3c.** The cyclocarbonylation of trimethylsilyl-substituted enynes was mediated most efficiently by the diphenyl complex **3a**. The optimal diene cycloisomerization catalyst was the dimethyl complex **3d**. The benefit of employing ligands that allow for tuning of steric or electronic parameters while maintaining overall reactivity is clearly demonstrated, and substituted

(33) For the preparation of bicyclic cyclopentenones with angular substituents from the corresponding trisubstituted olefins, see: Urabe, H.; Hideura, D.; Sato, F. *Org. Lett.* **2000**, *2*, 381−383.

(34) (a) Loebach, J. L.; Bennett, D. M.; Danheiser, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 9690−9691. (b) Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861−5869.

(35) Alimardanov, A.; Negishi, E.-i. *Tetrahedron Lett.* **1999**, *40*, 3839−3842.

(36) The following are representative examples demonstrating the utility of α-halocyclopentenones. *As componants of Pd-catalyzed coupling reactions:* (a) Negishi, E−i.; Owczarczyk, Z. R.; Swanson, D. R. *Tetrahedron Lett.* **1991**, *32*, 4453−4456. (b) Johnson, C. R.; Adams, J. P.; Braun, M. P.; Senanayake, C. B. W. *Tetrahedron Lett.* **1992**, *33*, 919−922. (c) Johnson, C. R.; Braun, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 11014−11015. (d) Magriotis, P. A.; Vourloumis, D.; Scott, M. E.; Tarli, A. *Tetrahedron Lett.* **1993**, *34*, 2071−2074. (e) Molander, G. A.; Hiersemann, M. *Tetrahedron Lett.* **1997**, *38*, 4347−4350. (f) Rossi, R.; Bellina, F.; Ciucci, D.; Carpita, A.; Fanelli, C. *Tetrahedron* **1998**, *54*, 7595−7614. Isoxazoline precursors: (g) Galli, C.; Marotta, E.; Righi, P.; Rosini, G. *J. Org. Chem.* **1995**, *60*, 6624−6626. Asymmetric dihydrofuran synthesis: (h) Arai, S.; Nakayama, K.; Suzuki, Y.; Hatano, K−i.; Shioiri, T. *Tetrahedron Lett.* **1998**, *39*, 9739−9742. Cyclopropanation substrates: (i) Arai, S.; Nakayama, K.; Hatano, K.-i.; Shioiri, T. *J. Org. Chem.* **1998**, *63*, 9572−9575. (j) Arai, S.; Nakayama, K.; Ishida, T.; Shiori, T. *Tetrahedron Lett.* **1999**, *40*, 4215−4218. Radical cyclization substrates: (k) Sha, C.-K.; Santhosh, K. C.; Tseng, C.-T.; Lin, C.-T. *J. Chem. Soc., Chem. Commun.* **1998**, 397−398.

(37) (a) Bright, A.; Malone, J. F.; Nicholson, J. K.; Powell, J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1971**, 712−713. (b) Grigg, R.; Malone, J. F.; Mitchell, T. R. B.; Ramasubbu, A.; Scott, R. M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1745−1754. (c) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett*, **1990**, 74−84. (d) Radetich, B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 8007−8008. (e) Heumann, A.; Moukhliss, M. *Synlett* **1998**, 1211−1212. (f) Yamamoto, Y.; Ohkishi, N.; Kameda, M.; Itoh, K. *J. Org. Chem.* **1999**, *64*, 2178−2179. (g) Widenhoefer, R. A.; Perch, N. S. *Org. Lett.* **1999**, *1*, 1103−1105. (h) Okamoto, S.; Livinghouse, T. *Organometallics* **2000**, *19*, 1449−1451.

aryloxide ligands are valuable in this respect. Monocyclopentadienyltitanium aryloxide complexes exhibit reactivity related to titanocene complexes and allow for the cyclization of more sterically demanding substrates.

Experimental Section

General Considerations. All manipulations involving air-sensitive materials were conducted in a Vacuum Atmospheres glovebox under an atmosphere of argon or nitrogen, or using standard Schlenk techniques under argon, in flame-dried glassware. Melting points were determined with a Mel-Temp II from Laboratory Devices. Celite was dried at 200 °C under vacuum for 24 h and stored in an argon-filled glovebox. Resealable Schlenk tubes were purchased from Kontes. Unless it is described as dry, Et_2O was used directly from a bottle stored on the benchtop. Toluene, THF, and dry Et_2O were purified by a solvent dispensing system,[38] involving passage through alumina columns under argon, or by distillation from sodium/benzophenone ketyl under argon. C_6D_6 was distilled from sodium. Anhydrous DMF was purchased from Aldrich and used without further purification. Cyclopentadienyltitanium trichloride ($CpTiCl_3$) and pentamethylcyclopentadienyltitanium trichloride (Cp^*TiCl_3) were purchased from Strem Chemicals, Inc., stored at −20 °C in an argon-filled glovebox, and used without further purification. 2,6-Diphenylphenol was purchased from Aldrich and used without further purification. Technical grade 2,6-diisopropylphenol was purchased from Aldrich, purified by vacuum distillation (72 °C, 0.4 mm), and stored in a Schlenk tube under argon. CO (scientific grade, minimum purity 99.997%) was purchased from MG Industries.

Cp(DIPP)$TiCl_2$ **3b**,[18] Cp(DM)$TiCl_2$ **3d**,[18] and **5e**[27] were prepared as previously described. Titanium complexes were stored and handled in an argon-filled glovebox. Flash chromatography was performed on E. M. Science Kieselgel 60 (230−400 mesh). Substrates were stored in the glovebox to prevent decomposition over long periods of time. Substrates that were transferred into the glovebox during periods of the year when the humidity in the laboratory was high were filtered through a plug of alumina (in the glovebox) to remove adventitious moisture. Unless otherwise indicated, yields refer to isolated yields of compounds of greater than 95% purity as estimated by ^1H NMR. Elemental analyses of organometallic compounds were performed by H. Kolbe, Mülheim an der Ruhr, Germany. Elemental analyses for all other compounds were performed by Atlantic Microlabs, Inc., Norcross, GA.

Monocyclopentadienyltitanium Dichloride 2,6-Diphenylphenoxide (3a). Triethylamine (0.95 mL, 6.8 mmol) was added to a solution of $CpTiCl_3$ (1.32 g, 6.0 mmol) and 2,6-diphenylphenol (1.50 g, 6.1 mmol) in dry Et_2O (200 mL) under argon at 25 °C, and the reaction mixture was stirred for 12 h. A white precipitate formed, and the Et_2O solution was cannula-filtered[39] into a dry Schlenk flask. The solids were rinsed with additional dry Et_2O (50 mL), and the resulting solution was cannula-filtered. The combined Et_2O solutions were concentrated in vacuo on a Schlenk line. Recrystallization in an argon-filled glovebox from a saturated solution of toluene layered with hexanes afforded 2.20 g (85% yield) of a yellow solid, mp 169−171 °C. ^1H NMR (300 MHz, C_6D_6): δ 7.52 (d, J = 7.0 Hz, 2 H); 7.30 (t, J = 7.8 Hz, 2 H); 7.15 (m, 8 H); 5.55 (s, 5 H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 164.1, 138.0, 133.3, 130.8, 130.5, 129.0, 127.6, 124.4, 120.7. IR (KBr): 3105, 3058, 3025, 2361, 2339. Anal. Calcd for $C_{23}H_{18}TiCl_2O$: C, 64.48; H, 4.24. Found: C, 64.48; H, 4.25.

Monocyclopentadienyltitanium Dichloride 2,6-Dimethoxyphenoxide (3c). In an argon-filled glovebox, KH (100 mg, 2.5 mmol) and 2,6-dimethoxyphenol (80 mg, 0.52 mmol) were combined in toluene (5 mL). After stirring the mixture for 1 h, a solution of $CpTiCl_3$ (130 mg, 0.59 mmol) in toluene (2 mL) was added. The mixture was stirred for 12 h, filtered through Celite with additional toluene, and concentrated in vacuo on a vacuum line in the glovebox. Crystallization from a saturated solution of toluene layered with hexanes afforded 126 mg (72% yield) of a red solid, mp 92−95 °C. ^1H NMR (500 MHz, C_6D_6): δ 6.68 (t, J = 8.2 Hz, 1 H); 6.24 (s, 5 H); 6.23 (d, J = 8.5 Hz, 2 H); 3.30 (s, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 151.6, 123.5, 123.1, 120.9, 106.0, 56.4. IR (KBr): 2935, 1590. Anal. Calcd for $C_{13}H_{14}TiCl_2O_3$: C, 46.43; H, 4.20; Cl, 20.82. Found: C, 46.23; H, 4.05, Cl, 21.08.

Pentamethylcyclopentadienyltitanium Dichloride 2,6-Diphenylphenoxide (4a). A resealable Schlenk tube was charged with NaH (105 mg, 4.38 mmol) and 2,6-diphenylphenol (366 mg, 1.49 mmol) in an argon-filled glovebox. The Schlenk tube was removed from the glovebox and attached to a Schlenk line. Under a flow of argon, toluene (10 mL) was added. The flask was sealed and heated at 100 °C for 30 min. The reaction mixture was cooled to 25 °C, and a solution of Cp^*TiCl_3 in toluene (10 mL) was added. The flask was sealed and heated at 100 °C for 20 h, then cooled and transferred to an argon-filled glovebox. The solution was filtered through a plug of Celite. The Celite was rinsed with additional toluene, and the combined solutions were concentrated in vacuo on a vacuum line in the glovebox to give an orange solid. The crude solid was dissolved in warm toluene (25 mL), layered with hexanes (75 mL), and cooled at −20 °C for 2 days. The solvent was decanted, and the crystals were rinsed with hexanes and dried in vacuo on a vacuum line in the glovebox to yield 360 mg (49%) of the title compound as orange needles, mp 222−226 °C. ^1H NMR (300 MHz, C_6D_6): δ 7.64 (d, J = 7.7 Hz, 4 H); 7.33 (t, J = 7.6 Hz, 4H); 7.20−7.14 (m, 4H); 6.92 (t, J = 7.3 Hz, 1H); 1.46 (s, 15H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 138.2, 134.6, 132.1, 131.4, 131.0, 128.7, 127.2, 123.4, 12.2. IR (KBr, cm^{-1}): 3055, 2911, 2371, 1403. Anal. Calcd for $C_{28}H_{28}TiCl_2O$: C, 67.46; H, 5.67. Found: C, 67.32; H, 5.61.

4,4-Bis(*tert*-butyldimethylsilyloxymethyl)-1-phenylhept-6-en-1-yne (5b). An Et_2O solution of DIBAL (14 mL, 1.0 M, 14 mmol) was added to a solution of 2-allyl-2-(3-phenylprop-2-ynyl)malonic acid diethyl ester[13] (2.04 g, 6.50 mmol) in dry Et_2O at 0 °C. The reaction mixture was allowed to warm to 25 °C. After 24 h, additional DIBAL (7 mL of a 1.0 M Et_2O solution, 7 mmol) was added. After an additional 48 h, the reaction mixture was quenched by the careful addition of 1.5 mL of MeOH. The resulting mixture was added to a separatory funnel with 1 M HCl and Et_2O. The layers were separated, and the Et_2O solution was rinsed with brine, dried with $MgSO_4$, filtered, and concentrated. A white solid was obtained by flash chromatography (2:1 Et_2O/hexanes). TBSCl (2.65 g, 17.4 mmol) was added to a solution of this material and imidazole (1.77 g, 26.0 mmol) in DMF (15 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was added to a separatory funnel with Et_2O. The Et_2O solution was rinsed twice with 1 M aqueous HCl, once with saturated aqueous $NaHCO_3$, and once with brine. The Et_2O solution was dried with $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (hexanes−3% Et_2O/hexanes) afforded 1.31 g (44% yield) of the title compound as a colorless oil. ^1H NMR (300 MHz, C_6D_6): δ 7.49 (dd, J = 7.0, 1.3 Hz, 2 H); 7.15 (m, 3 H); 5.97 (m, 1 H); 5.29 (dd, J = 17.0, 1.2 Hz, 1 H); 5.14 (dd, J = 9.9, 1.6 Hz, 1 H); 3.60 (dd, J = 18.4, 9.4, 4 H); 2.47 (s, 2 H); 2.38 (d, J = 7.3, 2 H); 0.98 (d, J = 1.0 Hz, 18 H); 0.09 (d, J = 3.9 Hz, 12 H). ^{13}C NMR (75 MHz, C_6D_6): δ 134.4, 131.9, 128.5, 124.72, 124.67, 118.2, 87.8, 64.1, 44.5, 35.9, 26.3, 22.5, 18.7, −5.16, −5.20. IR (neat): 3076, 2954, 2929, 2857, 1639, 1598. Anal. Calcd for $C_{27}H_{46}O_2Si_2$: C, 70.70; H, 10.12. Found: C, 70.68; H, 9.99.

9-Allyl-9-(3-(trimethylsilyl)-2-propynyl)fluorene (5c). A hexane solution of *n*-BuLi (5 mL, 1.61 M, 8 mmol) was added

(38) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H. *Organometallics* **1996**, *15*, 1518−1520.

(39) In this procedure, cannula filtration refers to transferring the liquid from a liquid/solid mixture, under argon, by a stainless steel cannula fitted on one end with a dry glass-fiber filter.

to a solution of 9-allylfluorene (1.6 g, 7.8 mmol) in THF (20 mL) at 0 °C. The resulting slurry was warmed to 25 °C and stirred for 2 h, producing a clear red solution. The solution was cooled to −78 °C and 3-bromo-1-(trimethylsilyl)-1-propyne (1.4 mL, 9.9 mmol) was added. The mixture was warmed to 25 °C and stirred for 12 h. The reaction mixture was quenched with H_2O, and the aqueous mixture was extracted with Et_2O. The organic layer was rinsed with brine, dried with $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (hexanes−1:24 Et_2O/hexanes) afforded 2.07 g (84% yield) of a pale yellow oil. ^{1}H NMR (300 MHz, C_6D_6): δ 7.55 (m, 2 H); 7.48 (m, 2 H); 7.19 (m, 4 H); 5.32 (ddt, J = 17.1, 9.9, 7.2 Hz, 1 H); 4.86 (m, 1 H); 4.67 (m, 1 H); 2.84 (d, J = 7.2 Hz, 2 H); 2.52 (s, 2 H); 0.14 (s, 9 H). ^{13}C NMR (75 MHz, C_6D_6): δ 149.4, 140.9, 133.8, 127.7, 127.3, 124.1, 120.1, 118.0, 104.9, 87.5, 52.5, 41.6, 30.8, 0.01. IR (neat): 3069, 2958, 2175, 1945, 1908. Anal. Calcd for $C_{22}H_{24}Si$: C, 83.50; H, 7.65. Found: C, 83.68; H, 7.59.

***N*-Allyl-*N*-(3-(trimethylsilyl)-2-propynyl)aniline (5f).** A hexane solution of *n*-BuLi (6.5 mL, 1.74 M, 11 mmol) was added to a solution of *N*-allylaniline (1.50 g, 11.3 mmol) in THF (20 mL) at −78 °C. After 5 min, 3-bromo-1-(trimethylsilyl)-1-propyne (1.6 mL, 11 mmol) was added, producing, over the course of 10 min, a red solution. The reaction mixture was warmed to 25 °C over 4 h and stirred for 8 h. The resulting solution was added to a separatory funnel with 1 N aqueous HCl (60 mL) and Et_2O (100 mL). The layers were separated and the Et_2O solution was rinsed twice with 1 N aqueous HCl, once with saturated aqueous $NaHCO_3$, and once with brine. The solution was dried with $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (two successive columns, first hexanes−1:19 Et_2O/hexanes, then hexanes−1:39 Et_2O/hexanes) afforded 1.9 g (70% yield) of a pale yellow oil. ^{1}H NMR (300 MHz, C_6D_6): δ 7.19 (m, 2 H); 6.78 (m, 3 H); 5.64 (ddt, J = 17.2, 10.2, 5.2 Hz, 1 H); 5.09 (dd, J = 17.2, 1.7 Hz, 1 H); 4.98 (dd, J = 10.2, 1.7 Hz, 1 H); 3.78 (s, 2 H); 3.72 (d, J = 5.2 Hz, 2 H); 0.12 (s, 9 H). ^{13}C NMR (75 MHz, C_6D_6): δ 148.8, 134.4, 129.3, 118.3, 116.3, 114.5, 103.0, 88.5, 53.7, 40.9, 0.0. IR (neat): 2958, 2169. Anal. Calcd for $C_{15}H_{21}NSi$: C, 74.03; H, 8.70. Found: C, 74.07; H, 8.71.

General Procedure for the Conversion of Enynes to Cyclopentenones. In an argon-filled glovebox, a dry resealable Schlenk tube was charged with the Cp(OAr)$TiCl_2$, toluene, and the substrate. The Schlenk tube was sealed, removed from the glovebox, and attached to a Schlenk line. Under a flow of argon, the solution was cooled to −78 °C and a solution of *n*-BuLi in hexanes was added dropwise. The reaction mixture was allowed to warm to 25 °C over the course of 2 h and stirred at 25 °C for 1 h. To prevent the formation of products resulting from the addition of butene to the substrate, it was important that the reaction was allowed to warm under a flow of argon, rather than in a sealed flask. The flask was subsequently sealed and attached to the CO source. The flask was evacuated and backfilled with CO at least three times, then filled to the desired pressure of CO. The Schlenk tube was sealed and heated at the temperature indicated for 24 h. *It is important to take appropriate safety precautions when using carbon monoxide, particularly at elevated pressure. All operations should be carried out in an efficient fume hood behind a blast shield.* After allowing the reaction mixture to cool to room temperature, the CO pressure was carefully released in the hood and the reaction mixture was quenched by the addition of 2−5 mL of Et_2O. Over the course of 15 min, a precipitate formed. The mixture was then filtered through a plug of silica gel with the aid of additional Et_2O, concentrated, and purified by flash chromatography.

7,7-Bis(*tert*-butyldimethylsilyloxymethyl)-3-phenyl-[3.3.0]bicyclooct-1-en-3-one (6b). The general procedure employing Cp(DME)$TiCl_2$ **3c** (10 mg, 0.03 mmol), *n*-BuLi (37 μL, 1.61 M, 0.06 mmol), toluene (2.4 mL), and CO (1 atm) was used to convert **7b** (77 mg, 0.17 mmol) to the title compound at 95 °C. Purification by flash chromatography (1:9 Et_2O/hexanes) afforded 64 mg (79% yield) of a white solid, mp 84 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.86 (m, 2 H); 7.24 (m, 2 H); 7.10 (m, 1 H); 3.47 (dd, J = 12.1, 9.5 Hz, 2 H); 3.23 (dd, J = 17.4, 9.5 Hz, 2 H); 2.48 (m, 3 H); 1.95 (m, 1 H); 1.83 (m, 1 H); 0.98 (s, 9 H); 0.85 (s, 9 H); 0.72 (m, 2 H); 0.09 (d, J = 1.1 Hz, 6 H); −0.09 (d, J = 1.5 Hz, 6 H). ^{13}C NMR (75 MHz, C_6D_6): δ 206.3, 181.6, 134.7, 132.5, 129.0, 128.8, 66.9, 66.0, 52.4, 43.3, 42.1, 36.4, 34.3, 26.1, 25.9, 18.5, 18.3, −5.3 (2C). IR (neat): 2954, 2928, 2896, 2856, 1704, 1650. Anal. Calcd for $C_{28}H_{46}O_2Si_2$: C, 69.09; H, 9.53. Found: C, 69.24; H, 9.79.

7,7-(9-Fluorenyl)-2-(trimethylsilyl)bicyclo[3.3.3]oct-1-en-3-one (6c). The general procedure employing Cp(DPP)$TiCl_2$ **3a** (172 mg, 0.40 mmol), *n*-BuLi (520 μL, 1.63 M, 0.85 mmol), toluene (8 mL), and CO (1.3 atm) was used to convert **5c** (120 mg, 0.38 mmol) to the title compound at 25 °C. Purification by flash chromatography (1:99−1:9 Et_2O/hexanes), followed by rinsing with hexanes, afforded 73 mg (56% yield) of a white solid, mp 190−192 °C (decomp). ^{1}H NMR (500 MHz, C_6D_6): δ 7.53 (d, J = 7.6 Hz, 2 H); 7.44 (d, J = 7.0 Hz, 1 H); 7.23−7.14 (m, 3 H); 7.06 (t, J = 7.3, 1 H); 3.46 (quintet, J = 8.9 Hz, 1 H); 2.93 (d, J = 16.8 Hz, 1 H); 2.69 (d, J = 17.7, 1 H); 2.49 (dd, J = 13.4, 7.3 Hz, 1 H); 2.24 (dd, J = 12.8, 8.5 Hz, 1 H); 1.82 (dd, J = 12.8, 10.7 Hz, 1 H); 1.51 (dd, J = 13.7, 8.5 Hz, 1 H); 0.32 (s, 9 H). ^{13}C NMR (125 MHz, C_6D_6): δ 192.0, 166.2, 154.5, 154.4, 140.0, 139.7, 136.7, 127.7, 127.5, 127.4, 123.4, 123.2, 120.1, 120.0, 102.9, 59.5, 53.7, 46.1, 45.8, 39.6, 1.5. IR (neat): 3556, 2962, 2280, 1618 cm^{-1}. Anal. Calcd for $C_{23}H_{24}OSi$: C, 80.20; H, 7.03. Found: C, 80.48; H, 7.01.

3-Phenyl-6-(trimethylsilyl)-3-azabicyclo[3.3.0]oct-5-en-7-one (6d). The general procedure employing Cp(DPP)$TiCl_2$ **3a** (35 mg, 0.10 mmol), *n*-BuLi (130 μL, 1.6 M, 0.20 mmol), toluene (4 mL), and CO (2.1 atm) at 95 °C was used to convert **5d** (70 mg, 0.29 mmol) to the title compound. Purification by flash chromatography (1:4 Et_2O/hexanes) afforded 73 mg (68% yield) of a white solid, mp 126−127 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.27 (dd, J = 8.5, 7.3 Hz, 2 H); 6.84 (t, J = 7.3 Hz, 1 H); 6.43 (d, J = 8.5, 2 H); 3.91 (d, J = 16.2 Hz, 1 H); 3.66 (d, J = 16.2 Hz, 1 H); 3.18 (t, J = 8.5 Hz, 1 H); 2.59 (m, 1 H); 2.22 (dd, J = 17.3, 6.9 Hz, 1H); 2.01 (dd, J = 10.4, 8.5 Hz, 1 H); 1.72 (dd, J = 17.3, 4.5 Hz, 1 H); 0.26 (s, 9 H). ^{13}C NMR (125 MHz, C_6D_6): δ 188.0, 147.8, 136.2, 129.5, 128.2, 117.4, 112.5, 51.4, 49.3, 45.6, 41.1, −1.3. IR (neat): 3366, 2959, 1691, 1622, 1598. Anal. Calcd for $C_{16}H_{21}NOSi$: C, 70.81; H, 7.81. Found: C, 70.80; H, 7.79.

3-Benzyl-8-methyl-6-(trimethylsilyl)-3-azabicyclo[3.3.0]-oct-5-en-7-one (6e). The general procedure employing Cp-(DPP)$TiCl_2$ **3a** (43 mg, 0.10 mmol), *n*-BuLi (130 μL, 1.63 M, 0.21 mmol), toluene (4 mL), and CO (2.1 atm) at 95 °C was used to convert **5e** (80 mg, 0.29 mmol) to the title compound. Purification by flash chromatography (1:5 Et_2O/hexanes to 1:3 Et_2O/hexanes) afforded 51 mg (59% yield) of a yellow oil. ^{1}H NMR (500 MHz, C_6D_6): δ 7.34 (d, J = 7.5 Hz, 2 H); 7.23 (t, J = 7.5 Hz, 2 H); 7.13 (m, 1 H); 3.81 (dd, J = 17.7, 1.2 Hz, 1 H); 3.43 (s, 2 H); 2.90 (t, J = 7.5 Hz, 1 H); 2.85 (dd, J = 17.7, 2.1 Hz, 2 H); 2.54 (m, 1 H); 1.84 (dq, J = 7.3, 4.6 Hz, 1 H); 1.47 (dd, J = 11.0, 8.2, 1 H); 1.09 (d, J = 7.3 Hz, 3 H); 0.23 (s, 9 H). ^{13}C NMR (125 MHz, C_6D_6): δ 212.9, 190.0, 139.2, 134.2, 128.8, 128.7, 127.5, 60.0, 57.3, 55.9, 54.9, 48.0, 13.6, −1.3. IR (neat): 2961, 2791, 1702, 1621. Anal. Calcd for $C_{18}H_{25}NOSi$: C, 72.20; H, 8.42. Found: C, 72.33; H, 8.44. The relative stereochemistry was anticipated to be *trans* based on the geometry of the starting material, and this was confirmed by an NOE difference experiment indicating a 4.4% enhancement of the methine resonance (δ 2.54) upon irradiation of the methyl resonance (δ 1.09).

9-But-2-ynyl-9-(3-methylbut-2-enyl)fluorene (8). A hexane solution of *n*-BuLi (31 mL, 1.6 M, 50 mmol) was added to a solution of fluorene (8.3 g, 50 mmol) in THF (100 mL) at −78 °C. The resulting slurry was warmed to 25 °C and stirred for 30 min, producing a clear solution. The solution was

recooled to −78 °C, and 1-bromo-2-butyne (4.4 mL, 50 mmol) was added. The reaction mixture was warmed to 25 °C and stirred for 12 h. Saturated aqueous NH_4Cl was added, and the mixture was extracted with Et_2O (approximately 400 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated to afford a yellow oil. This material was purified by vacuum distillation (120−130 °C, 0.01 mm) to provide 11 g (quantitative yield) of 9-but-2-ynylfluorene as a white solid. To a solution of this compound (3.3 g, 15 mmol) in THF at 0 °C was added a hexane solution of *n*-BuLi (10.5 mL, 1.6 M, 15 mmol). The reaction mixture was allowed to warm to 25 °C, stirred for 1 h, and then cooled to −78 °C. A solution of the 3-methyl-2-butenyl methanesulfonate (generated in situ, immediately prior to use, from 3-methyl-2-butene-1-ol (3 mL, 30 mmol), Et_3N (4.5 mL, 32 mmol), and MsCl (2.3 mL, 30 mmol) in THF (60 mL)) was added to the 9-but-2-ynylfluorenyllithium solution. The reaction mixture was warmed to 25 °C and stirred for 12 h. Saturated aqueous NH_4Cl was added, and the mixture was extracted with Et_2O (200 mL). The Et_2O solution was rinsed with brine, dried with $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (hexanes−1:19 Et_2O/hexanes) afforded 1.5 g (34% yield) of a viscous oil. ^{1}H NMR (500 MHz, C_6D_6): δ 7.57 (m, 4 H); 7.20 (m, 4 H); 4.89 (t, J = 7.3 Hz, 1 H); 2.92 (d, J = 7.0 Hz, 2 H); 2.60 (q, J = 2.4 Hz, 2 H); 1.46 (t, J = 2.4 Hz, 3 H); 1.39 (s, 3H); 1.31 (d, J = 0.9 Hz, 3 H). ^{13}C NMR (125 MHz, C_6D_6): δ 150.4, 140.9, 133.5, 128.3, 127.6, 127.2, 124.1, 120.2, 120.1, 77.7, 76.9, 53.2, 36.2, 29.7, 25.7, 18.1, 3.3. IR (neat): 2915, 1448. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.15; H, 7.90.

Titanacyclopentene (9). In an argon-filled glovebox, a resealable Schlenk tube was charged with Cp(DIPP)$TiCl_2$ **3b** (173 mg, 0.50 mmol), enyne **8**, and toluene (20 mL). The flask was removed from the box, attached to a Schlenk line, and cooled to −78 °C. Under a flow of argon, a hexane solution of *n*-BuLi (0.64 mL, 1.63 M, 1.05 mmol) was slowly added. The solution was stirred at −78 °C for 1.5 h, slowly warmed to 25 °C, and stirred for 2 h, producing a dark brown solution. The reaction mixture was concentrated in vacuo on a Schlenk line, and the flask was sealed and transferred to the glovebox. The resulting residue was dissolved in pentane, filtered through a pad of Celite, and concentrated to afford 289 mg (95% yield) of a brown solid, mp 132−133 °C, that was 90% pure by ^{1}H NMR. Efforts to purify this compound resulted in material of diminished purity; the complex was always cleanest immediatly upon isolation. Furthermore, attempts at purification by chromatography in the glovebox using alumina (dried at 200 °C under high vacuum for 24 h) resulted in the isolation of compund **10H**. Although the presence of small amounts of impurities was detected by NMR, they did not appear to complicate the interpretation of spectra. ^{1}H NMR (500 MHz, C_6D_6): δ 7.72 (d, J = 7.5 Hz, 1 H); 7.62 (d, J = 6.5 Hz, 1 H); 7.59 (d, J = 7.5 Hz, 1 H); 7.24 (m, 3 H); 7.14 (m, 2 H); 7.10 (t, J = 7.8 Hz, 1 H); 7.01 (t, J = 7.5 Hz, 1 H); 6.91 (t, J = 7.8 Hz, 1 H); 4.54 (m, 1 H); 3.35 (m, 1 H); 3.43 (m, 1 H); 3.02 (d, J = 17.3 Hz, 1 H); 2.89 (d, J = 17.3 Hz, 1 H); 2.49 (t, J = 12.0, 1 H); 2.22 (ddd, J = 12.3, 7.8, 2.3 Hz, 1 H); 1.96 (s, 3 H), 1.38 (s, 3 H); 1.30 (d, J = 7.0 Hz, 3 H); 1.19 (d, J = 6.5 Hz, 3 H); 0.83 (s, 3 H). ^{13}C NMR (125 MHz, C_6D_6): δ 201.3, 160.8, 153.0, 150.9, 144.5, 141.2, 139.7, 136.8, 128.3, 128.1, 127.6, 127.5, 127.4, 123.9, 123.4, 122.8, 121.3, 120.2, 120.0, 113.6, 72.4, 52.5, 46.5, 46.0, 38.9, 29.0, 26.5, 24.5, 23.7. IR (KBr): 2959, 1654, 1634. HRMS (m/z): M^+ calcd for $C_{39}H_{44}TiO$, 576.2872; found, 576.2862. The 1D ^{1}H and ^{13}C NMR peaks for the metallacycle were assigned, as shown in Figure 6, based on a series of NMR experiments including gCOSY, DEPT135, HMQC, HMBC, and NOE difference experiments.[32] Indicative HMBC cross-peaks were observed as follows: the methyl proton resonances at δ 1.96 with the olefin carbon resonances at δ 201.2, 144.5; the proton resonances at δ 2.89, 3.02 with the carbon resonance at δ 144.5; the proton resonance at δ 4.45 with the carbon resonances at δ 46.0, 72.4, 144.5. An NOE enhancement of the proton resonance at δ 7.72 was observed upon irradiation at δ 4.45 and vice versa. However, irradiation at δ 4.45 had no influence on the resonance at δ 7.24. Irradiation at δ 7.72 also resulted in enhancement of the resonance at δ 6.91.

9-*cis*-2-Butenyl-9-(3-methyl-2-butenyl)fluorene (10H and 10D). Metallacycle **9** was prepared as described from enyne **8** (30 mg, 0.10 mmol) and Cp(DIPP)$TiCl_2$ **3b** (34 mg, 0.10 mmol). The reaction mixture was divided into two equal portions, and each was treated with 1 N aqueous HCl (200 μL) or DCl (20 wt % % in D_2O, 200 μL) at 0 °C and warmed to room temperature. The mixture was added to H_2O and extracted with Et_2O. The Et_2O solution was dried with $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (hexanes−1:50 Et_2O/hexanes) provided 5 mg (35% yield) of the title compound as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6): δ 7.56 (dd, J = 7.0, 1.5 Hz, 2 H); 7.32 (dd, J = 7.0, 1.5 Hz, 2 H); 7.18 (m, 4 H); 5.15 (m, 1 H); 5.01 (m, 1 H); 4.85 (tt, J = 7.5, 1.5 Hz, 1 H); 2.72 (d, J = 7.0 Hz, 2 H); 2.69 (d, J = 7.0 Hz, 2 H); 1.38 (s, 3 H); 1.36 (d, J = 6.0 Hz, 3 H); 1.32 (s, 3 H). ^{13}C NMR (125 MHz, C_6D_6): δ 13.1, 18.0, 25.7, 36.5, 38.0, 55.0, 120.0, 120.2, 123.7, 125.6, 126.0, 127.1, 127.3, 133.2, 141.4, 150.5. HRMS (m/z): M^+ calcd for $C_{22}H_{24}$, 288.1873; found, 288.1871. The ^{1}H NMR of **10D** matched that for **10H**, with the absence of peaks at 5.15 and 5.01 ppm.

1-Ethylidene-4,4-(9-fluorenyl)-2-isopropylcyclopentane (11). Metallacycle **9** was prepared as described from enyne **8** (55 mg, 0.19 mmol) and Cp(DIPP)$TiCl_2$ **3b** (68 mg, 0.20 mmol) in toluene (8 mL). TfOH from a freshly opened ampule (36 μL, 0.40 mmol) was added to the solution at −78 °C, and the reaction mixture was stirred for 5 h. The reaction mixture was warmed to room temperature and added to a separatory funnel with H_2O and Et_2O (40 mL). The layers were separated, and the organic solution was rinsed with saturated aqueous $NaHCO_3$, dried with $MgSO_4$, filtered, and concentrated. Purification by column chromatography (hexanes; compound **11** is the least polar component of the product/ligand mixture) provided 10 mg (18% yield) of the title compound as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6): δ 7.62 (m, 2 H); 7.53 (d, J = 7.3 Hz, 1 H); 7.30−7.17 (m, 5 H); 5.40 (m, 1 H); 2.96 (m, 1 H); 2.66 (dd, J = 16.5, 2.4 Hz, 1 H); 2.47 (d, J = 2.5 Hz, 1 H); 2.06 (dd, J = 12.9, 10.5 Hz, 1 H); 1.98 (m, 1 H); 1.70 (ddd, J = 12.9, 8.2, 1.8 Hz, 1 H); 1.51 (d, J = 6.7 Hz, 3 H); 0.91 (d, J = 7.0 Hz, 3 H); 0.85 (d, J = 7.0 Hz, 3 H). ^{13}C NMR (125 MHz, C_6D_6): δ 154.7, 154.2, 151.7, 145.6, 140.6, 139.7, 127.7, 127.5, 127.4, 127.3, 123.5, 122.9, 120.0, 117.0, 55.8, 49.6, 42.1, 39.7, 31.7, 21.2, 16.9, 15.0. IR (neat): 2910. HRMS (m/z): M^+ calcd for $C_{22}H_{24}$, 288.1873; found, 288.1864.

4,4-(9-Fluorenyl)-1-methyl-2-methylenecyclopentane (12). In an argon-filled glovebox, Cp(DM)$TiCl_2$ **3d** (18 mg, 0.06 mmol), 9,9-diallylflourene[40] (87 mg, 0.35 mmol), and THF (2.4 mL) were combined in a resealable Schlenk tube. The flask was removed from the glovebox, attached to a Schlenk line, and cooled to −78 °C. An Et_2O solution of cyclohexyl-MgCl (60 μL, 2.0 M, 0.12 mmol) was added; the solution was allowed to warm to 25 °C over the course of 2 h and was stirred at room temperature for 1 h. Concentration of the crude reaction mixture and purification by flash chromatography (hexanes) yielded 78 mg (90% yield) of the cyclized product as a white solid. The ^{1}H NMR was consistent with reported data.[8]

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Supporting Information Available: Listings of X-ray structural data for complexes **3a**, **3c**, and **4a**. Heteronuclear and ^{1}H NMR spectra for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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