Titanium Aryloxide Catalyzed Cross-Coupling and Oligomerization Reactions Involving 1,3-Cyclohexadiene, 1,3-Cyclooctadiene, and α-Olefins

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Abstract: The dimerization/oligomerization and cross coupling of 1,3-cyclohexadiene (1,3-CHD) with α-olefins can be achieved using a variety of titanium aryloxide catalysts. The titanabicyclic compound [Ti($OC_6H_3Ph_4$-2,3,5,6)$_2${$CH_2(C_6H_{10})CH_2$}] initiates the rapid, non-Diels−Alder catalytic dimerization of 1,3-CHD to produce exclusively *threo*-5-(3-cyclohexenyl)-1,3-cyclohexadiene. Following dimerization of the majority of 1,3-cyclohexadiene into **8**, the titanium catalyst then isomerizes (1,5-shift) **8** into 1-(3-cyclohexenyl)-1,3-cyclohexadiene **9** and eventually into a 70/30 mixture (GC analysis) of **9** and 2-(3-cyclohexenyl)-1,3-cyclohexadiene **10**. Further cross coupling of dimers **8**−**10** with themselves and 1,3-CHD leads to trimers (C_{18} species) and tetramers (C_{24}). This reaction can also be catalyzed by the dichlorides [Ti$(OAr)_2Cl_2$] (OAr = 2,6-diphenyl-, 2,3,5,6-tetraphenyl-, 2,6-diphenyl-3,5-dimethyl-, and 2,6-di-isopropyl-phenoxide) and [Cp(OAr)$TiCl_2$] (OAr = 2,6-diphenyl-3,5-dimethyl-phenoxide) activated with 2 equiv of *n*-butyllithium (Bu^nLi). In the case of the catalyst system [Ti$(OAr)_4$] or [Ti$(OAr)_2Cl_2$] (OAr = 2,6-dimethylphenoxide), activation with 2 equiv of Bu^nLi leads to isomeric mixtures of trimers and tetramers of 1,3-CHD with detectable amounts of pentamers following dimerization. The dimerization product is argued to originate via initial coupling of 1,3-CHD at the Ti metal center to produce 9-titana-octahydrofluorenes. A 1,3-metal shift followed by β-hydrogen abstraction/elimination accounts for the observed regio- and stereochemistry. When the α-olefin $Me_3SiCH{=}CH_2$ is added to 1,3-CHD, these titanium systems generate the cross-coupled product 5-(β-trimethylsilylethyl)-cyclohexa-1,3-diene followed by the formation of *trans*-5,6-bis(β-trimethylsilylethyl)-cyclohexa-1,3-diene. A mechanism involving initial coupling of the 1,3-CHD and $Me_3SiCH{=}CH_2$ at titanium prior to a 1,3-metal shift and β-hydrogen abstraction/elimination from the initial cyclohexadiene ring is invoked. In contrast cross-coupling of cycloocta-1,3-diene (1,3-COT) with α-olefins $RCH{=}CH_2$ (R = Ph, Bu^n, $SiMe_3$) leads to *trans*-3-(β-alkylvinyl)-cyclooctenes. In this case the reaction is proposed to proceed via similar titanacycles with β-hydrogen abstraction taking place from the alkyl tether instead of the cyclooctene ring.

Introduction

The ability of transition metal compounds to carry out the facile, selective coupling and/or oligomerization of unsaturated organic substrates is a major feature of organometallic catalysis.[1] A dominant endeavor of organometallic chemistry is to understand how the structure and reactivity of intermediate metal complexes can account for (or indeed control) the regio- and stereochemistry of the final products. In the case of olefins the transition metal-catalyzed polymerization of ethylene and 1-alkenes is a reaction that has received considerable study.[2] Varying the structure of the metal catalysts can now accurately control the morphology of the ensuing polymer.[3] One chain termination step in these systems that may ultimately control the polymer molecular weight involves the β-hydrogen abstraction processes. An alternative pathway for the utilization of olefins involves their coupling at low valent metal centers to produce metallacyclopentane compounds.[4] Although typically slow, β-hydrogen abstraction/elimination from such metallacycles offers a possible pathway for the selective dimerization of olefins. A recent study by our group has shown that titanacyclopentane rings supported by aryloxide ligation exhibit significant thermal stability.[5] At elevated temperatures such compounds act as catalysts for the slow dimerization of α-olefins. We wish to discuss in detail here our discovery that the decomposition of titanacyclopentane rings formed by coupling of olefins is accelerated greatly by the presence of α-vinyl substitutents. This study explores the synthetic utility of this catalysis as well as a mechanistic study of how the organometallic intermediates control the observed product regio- and stereochemistry.[6]

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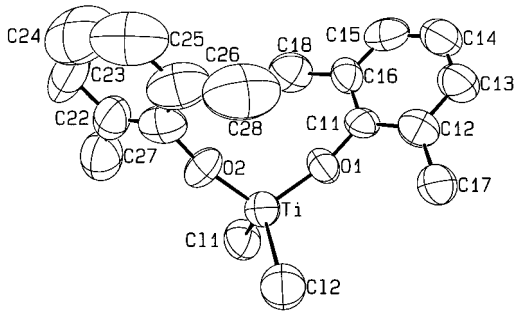


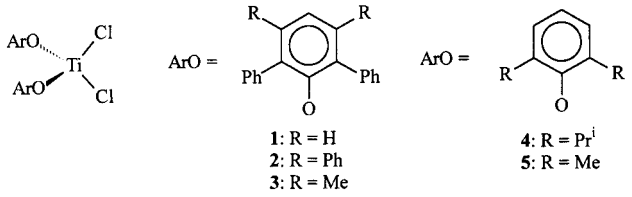
Figure 1. ORTEP view of $[Ti(OC_6H_3Me_2\text{-}2,6)_2Cl_2]$ **5**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[Ti(OC_6H_3Me_2\text{-}2,6)_2Cl_2]$ **5**

Ti−O(1)	1.734(7)	Ti−O(2)	1.736(8)
Ti−Cl(1)	2.192(4)	Ti−Cl(2)	2.211(4)
O(1)−Ti−O(2)	109.1(4)	Cl(1)−Ti−Cl(2)	111.0(2)
O(1)−Ti−Cl(1)	109.4(3)	O(1)−Ti−Cl(2)	108.1(3)
O(2)−Ti−Cl(1)	109.2(3)	O(2)−Ti−Cl(2)	110.1(3)
Ti−O(1)−C11)	167.3(7)	Ti−O(2)−C(21)	168.9(8)

Results and Discussions

Oligomerization of 1,3-Cyclohexadiene (1,3-CHD). The titanium dichloride compounds $[Ti(OAr)_2Cl_2]$ (**1**−**5**) prove to



be excellent starting materials for carrying out stoichiometric and catalytic organic transformations.[7,8]

All of the molecules appear to be monomeric in the solid state. The molecular structure of the 2,6-di-phenylphenoxide[9] as well as that of the 2,6-dimethylphenoxide (Figure 1, Table 1)[9] highlight this and contrast with the dimeric structure adopted by the phenoxide bridged molecule $[Ti_2(\mu\text{-}OPh)_2(OPh)_2Cl_4]$.[10] The first four compounds (**1**−**4**) are isolated by simple addition of 2 equiv of the corresponding phenol to $TiCl_4$, while **5** was obtained by mixing previously reported $[Ti(OAr)_4]$ **6** with $[TiCl_4]$.

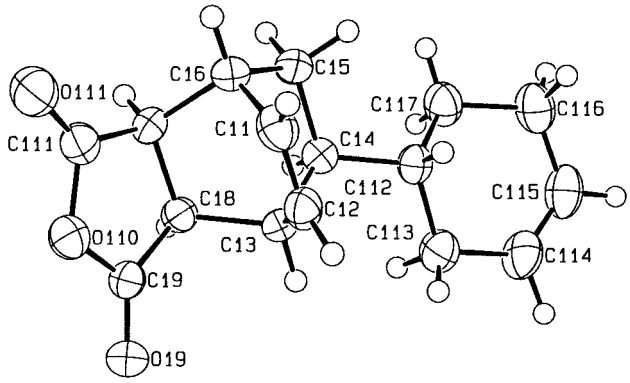
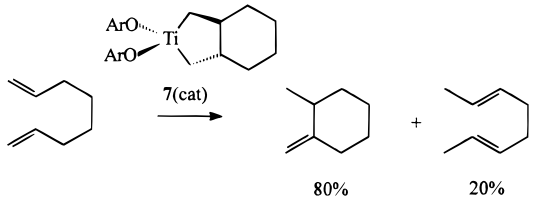
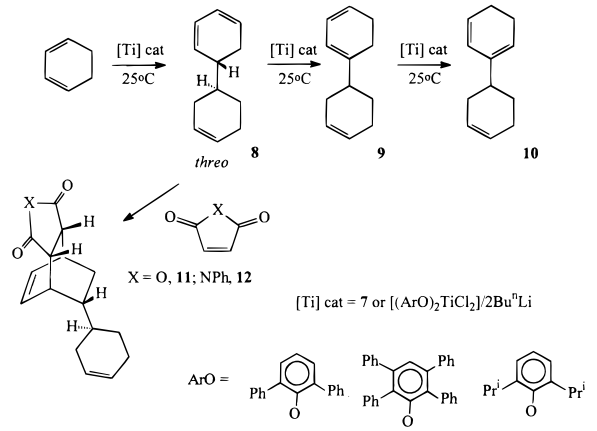


Figure 2. ORTEP view of **11**, the maleic anhydride adduct of **8**.

Scheme 1



Scheme 2



The titanabicyclic compound $[Ti(OC_6HPh_4\text{-}2,3,5,6)_2\{CH_2\text{-}(C_6H_{10})CH_2\}]$ **7** can be obtained by sodium amalgam (2 equiv of Na per Ti) reduction of **2** in the presence of 1,7-octadiene.[5] At 100 °C **7** is a catalyst for the cyclization of 1,7-octadiene to produce 2-methylmethylenecyclohexane at a rate of ∼1 equiv Ti^{-1} h^{-1} at 100 °C (Scheme 1). In contrast to these slow coupling reactions, when **7** is added to a hydrocarbon solution of 1,3-cyclohexadiene (1,3-CHD), rapid, exothermic production of the dimer *threo*-5-(3-cyclohexenyl)-1,3-cyclohexadiene **8** takes place (Scheme 2). Following dimerization of the majority of 1,3-CHD into **8**, the reaction mixture then causes the isomerization (1,5-hydrogen shift) of **8** into 1-(3-cyclohexenyl)-1,3-cyclohexadiene **9** and eventually into a 70/30 mixture of **9** and 2-(3-cyclohexenyl)-1,3-cyclohexadiene **10** (Scheme 2). The build up of trimers (C_{18} species) and tetramers (C_{24} species) of 1,3-CHD is also observed. These were identified by GC/MS analysis and shown to be present as mixtures of isomers. Both the regiochemistry and *threo*-stereochemistry of **8** were confirmed by formation of the maleic anhydride and *N*-phenylmaleamide adducts **11** and **12** (Scheme 2) and a single-crystal X-ray diffraction analysis of **11** (Figure 2, Table 2). The catalytic dimerization and oligomerization of 1,3-CHD can also be achieved using the pre-catalysts $[(ArO)_2TiCl_2]$ (**1**−**5**) activated with 2 equiv of *n*-butyllithium (Bu^nLi). Previous work with the

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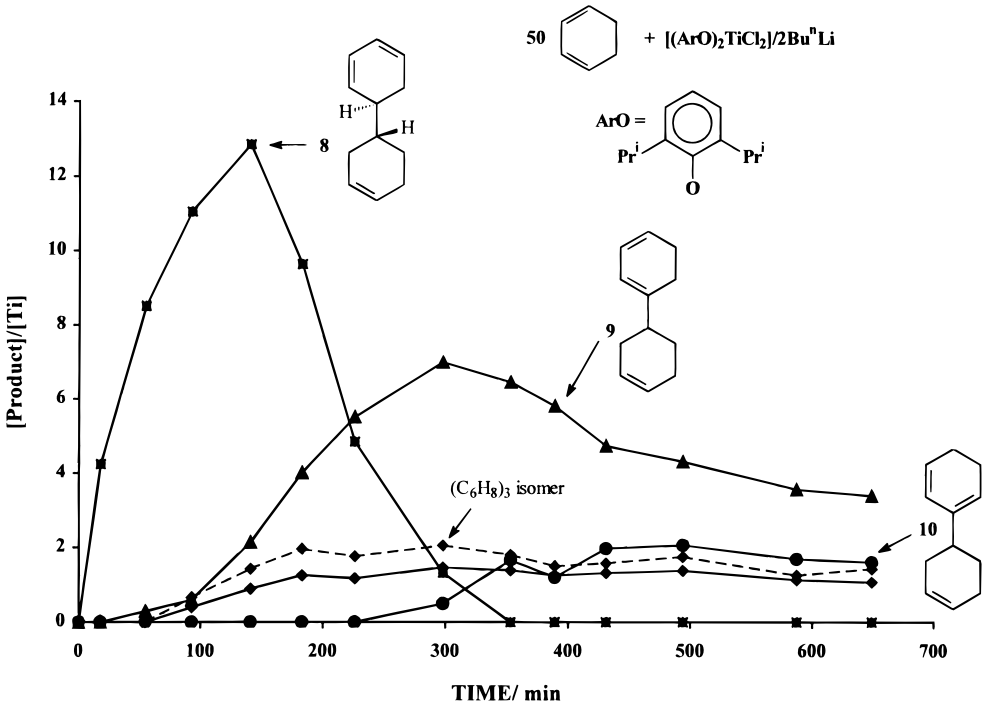

Figure 3. Reaction profile for the oligomerization of 1,3-CHD by **4**/2Bu^{n}Li. Reaction mixture: Ti, 0.21 mmol; 1,3-CHD, 10.5 mmol; mesitylene marker, 0.73 mmol; C_6H_6 solvent, total volume 10 mL.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $C_{16}H_{18}O_3$ **11**

C(112)−C(113)	1.518(4)	C(113)−C(114)	1.508(3)
C(114)−C(115)	1.312(4)	C(115)−C(116)	1.479(4)
C(116)−C(117)	1.528(3)	C(117)−C(112)	1.535(4)
C(212)−C(213)	1.521(3)	C(213)−C(214)	1.509(3)
C(214)−C(215)	1.318(4)	C(215)−C(216)	1.482(4)
C(216)−C(217)	1.525(4)	C(217)−C(212)	1.532(3)

2,6-diphenylphenoxides indicates that this reaction mixture produces an intermediate 1-butene complex.[5] Analogous reactivity has been proposed for the activation of $[Cp_2ZrCl_2]$ with Bu^{n}Li (2 equiv) (the "Negishi Method").[12] Recently, however, Harrod et al. have shown that the "activation" of $[Cp_2ZrCl_2]$ with Bu^{n}Li in the absence of added unsaturated reactant is a complex reaction leading to a variety of products.[13]

The product mixtures obtained by using either titanacycle **7** or **2**/2Bu^{n}Li as catalysts (precursors) are identical. There is, however, a difference in both reaction rate and product distribution when the aryloxide ligand is varied. With the three precursors **1**−**3** activated with Bu^{n}Li the formation of dimer **8** is too fast (>500 equiv of 1,3-CHD oligomerized per hour) for kinetic monitoring of the reaction. However, in the case of the 2,6-di-isopropylphenoxide **4** activated by Bu^{n}Li, the reaction is slow enough that the reaction profile can be reasonably monitored by GC analysis. In Figure 3 is shown a plot of products (as equivalents per Ti) produced when [**4**/2Bu^{n}Li] in benzene solution oligomerizes 50 equiv of 1,3-CHD. Following the build up of dimer **8** it can be seen that isomerization to **9** occurs along with the buildup of isomeric trimers (5 isomers detected by GC/MS, only the two major ones plotted in Figure 3). The buildup of trimers, which must arise by coupling of dimers with 1,3-CHD, halts after all 1,3-CHD is consumed. The isomerization of **8** into **9** and **10** is then completed. The slow decrease in the amount of **9** and **10** present can be accounted for by self-coupling to form small amounts of tetramers (at least 11 isomers detected by GC) which are not plotted. In Table 3 is collected the dimer, trimer, tetramer, and pentamer distribution produced when **1**/2Bu^{n}Li, **4**/2Bu^{n}Li, or **5**/2Bu^{n}Li oligomerize 100 equiv of 1,3-CHD. After 1 h **1**/2Bu^{n}Li completely oligomerizes the 1,3-CHD predominantly to dimers. Over the next 23 h the amount of trimers remains constant (all 1,3-CHD exhausted), while dimers are partially converted to tetramers. In the case of the catalyst systems **5**/2Bu^{n}Li or **6**/2Bu^{n}Li trimers begin to form early on in the reaction, and eventually all intermediate dimer that is produced is converted into a mixture of trimers, tetramers, and pentamers. We believe that in this case the small size of the 2,6-dimethylphenoxide ligands facilitates coupling of substituted 1,3-cyclohexadienes more readily than the bulkier ligands, and this is discussed in more detail below.

Table 3. Final Product Distribution (%) for the Oligomerization of 1,3-CHD by [Ti]/2Bu^{n}Li[a]

[Ti]	$(C_6H_8)_2$	$(C_6H_8)_3$	$(C_6H_8)_4$	$(C_6H_8)_5$
$[Ti(OC_6H_3Ph_2\text{-}2,6)_2Cl_2]$ **1**[b]	68	29	3	
$[Ti(OC_6H_3Ph_2\text{-}2,6)_2Cl_2]$ **1**	54	25	21	
$[Ti(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2]$ **4**	24	65	11	
$[Ti(OC_6H_3Me_2\text{-}2,6)_2Cl_2]$ **5**	3	67	28	2
$[CpTi(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)Cl_2]$	53	31	16	

[a] 0.13 mmol [Ti]; 0.26 mmol Bu^{n}Li; 13 mmol 1,3-CHD; 3 mL of C_6H_6; 24 h unless stated. [b] 1 h.

The reaction mixture $[Cp_2TiCl_2]$/2Bu^{n}Li demonstrates very little activity for the oligomerization of 1,3-CHD. However, the precursor $[CpTi(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)Cl_2]$[14] does show activity and leads to a reaction mixture similar to that produced by **1**/2Bu^{n}Li after 24 h (Table 3).

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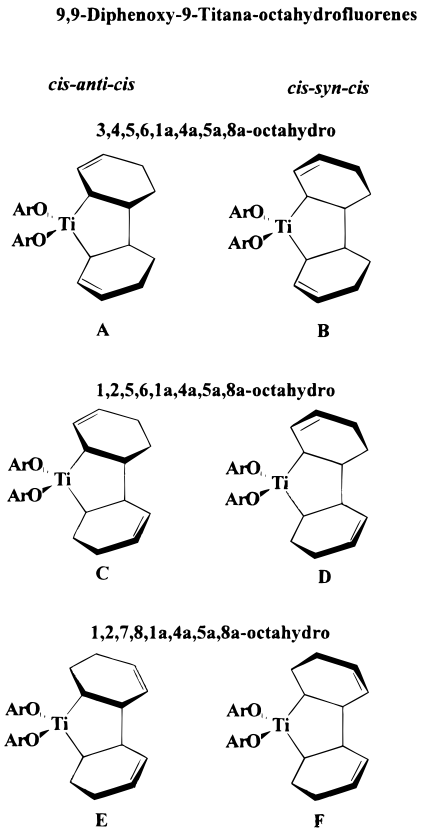
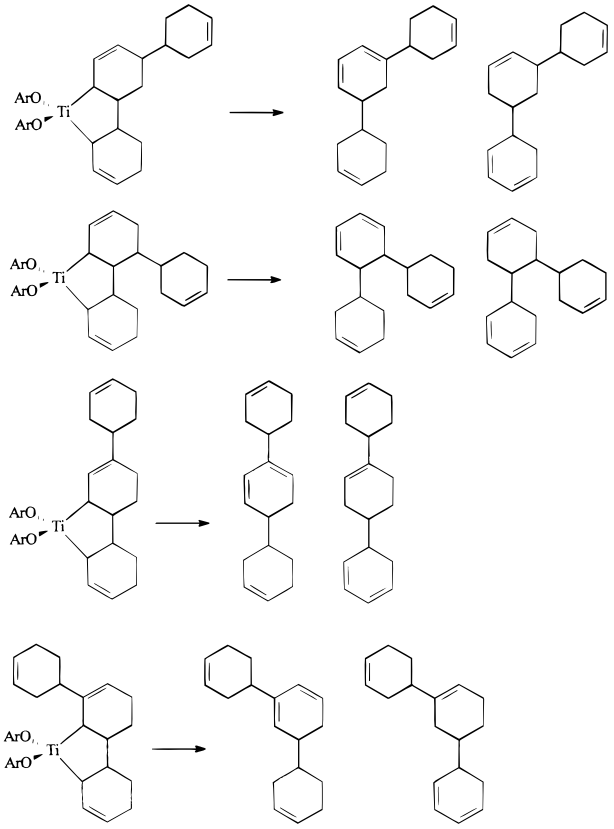
Scheme 3



Scheme 4



Mechanism of 1,3-CHD Oligomerization. An interesting feature of the initial dimerization is that it produces only the *threo*-stereoisomer of the least thermodynamically stable 5-(3-cyclohexenyl)-1,3-cyclohexadiene **8**. Furthermore, this molecule has never been reported in any other metal-catalyzed reaction or by the thermal or chemical dimerization of 1,3-CHD.[14] The coupling of two 1,3-CHD molecules at a titanium metal center can produce six isomeric 9,9-diphenoxy-9-titana-octahydrofluorenes (Scheme 3). Two of these isomers, **E** and **F**, do not have the potential for π-allylic stablization, while two of them, **A** or **B,** could possibly form bis(π-allylic) species. In all of these six titanacycles the central β-hydrogen atoms of the five-membered ring are all *trans* to the metal center. Hence, abstraction of these hydrogens is disallowed. Metallacycles **C**−**F** do contain accessible β-hydrogens. However, abstraction/elimination of these hydrogens will only lead initially to 1,4-cyclohexadiene products. The observed dimer **8** can be obtained by first allowing a 1,3-shift of the metal within **A** or **B**. This shift results in an overall ring expansion (titanacycloheptene) which makes available a new β-hydrogen for abstraction. Following this sequence of events leads to the conclusion that the observed *threo*-stereochemistry arises exclusively via the *cis-anti-cis* metallacycle **A**. A reaction proceeding via *cis-syn-cis* isomer **B** would generate an *erythro* product. A similar 1,3-shift for isomers **C** and **D** would lead, after abstraction/elimination to 5-(2-cyclohexenyl)-1,3-cyclohexadiene, the *erythro* isomer of which has previously been isolated by photodimerization of 1,3-CHD. In this case the *cis-anti-cis* intermediate **C** would lead to the *erythro*-isomer.

An alternative pathway for the formation of **8** must also be considered. The isomerization of 1,3-cyclohexadienes has been observed following the titanium aryloxide catalyzed (2 + 2 + 2) cyclization of an olefin with 2 equiv of alkyne.[15] It has been argued that such isomerizations occur via metal-mediated 1,5-hydrogen shifts within η^4-cyclohexadiene complexes. In the case of the group 5 metals Nb and Ta, the coordination of 1,3-cyclohexadiene to d^2-[M(OAr)$_3$] metal fragments has been shown to lead to stable complexes whose structural parameters are consistent with a metallanorbornene resonance form.[16] These isomerization reactions proceed via cyclohexadienyl hydride intermediates. Hence, coupling of 1,3-CHD might take place by insertion of a 1,3-CHD molecule into this intermediate hydride. However, this pathway does not account for the observed regiochemistry and furthermore does not explain why only the *threo* isomer. Also arguing against hydride intermediates is the previously reported dimerization of acyclic dienes where formation of analogous hydrides would be impossible.[17]

The data shown in Figure 3 shows that following formation of a significant amount of **8**, the reaction mixture begins to catalyze its isomerization to **9** (and eventually **10**). This requires **8** to re-enter the metal coordination sphere. At this point there appear to be a number of options depending on the bulk of the aryloxide ligand. Isomerization to produce **9** can occur. Alternatively the metal bound dimers **8**, **9** (or eventually **10** when formed) can couple with any 1,3-CHD in solution to produce trimers. A third possibility that is favored with smaller aryloxide ligands is coupling of dimers (or even trimers) to produce tetramers (pentamers). Many regio- and stereoisomers are possible for the trimer and tetramer of 1,3-CHD. In Scheme 4 are shown some of the regio-isomeric trimers that can be formed from the dimers **8**−**10** using the mechanistic pathway described for the initial dimerization of 1,3-CHD. Only coupling at the

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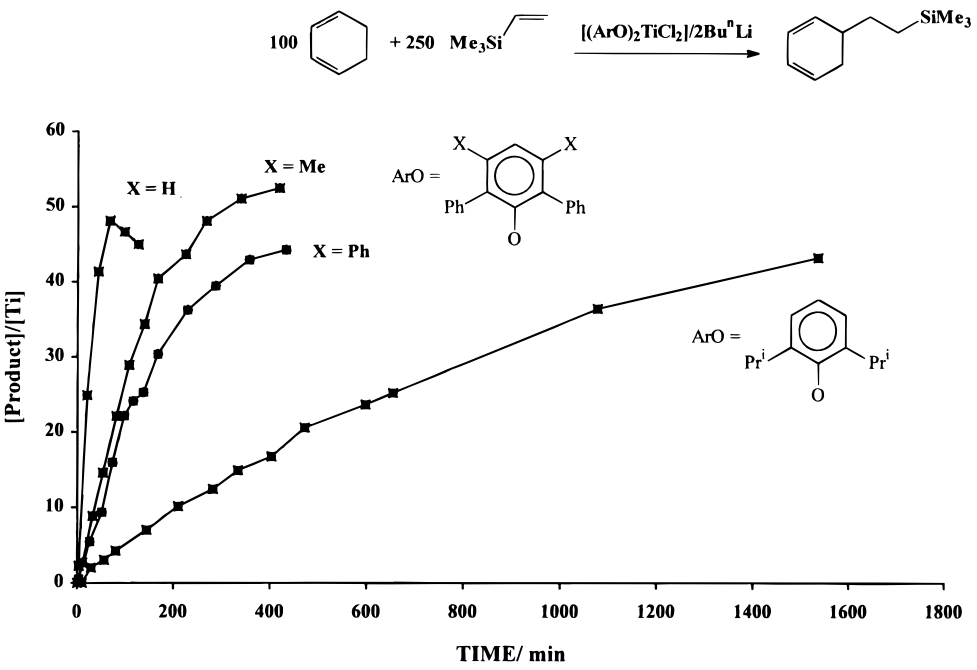
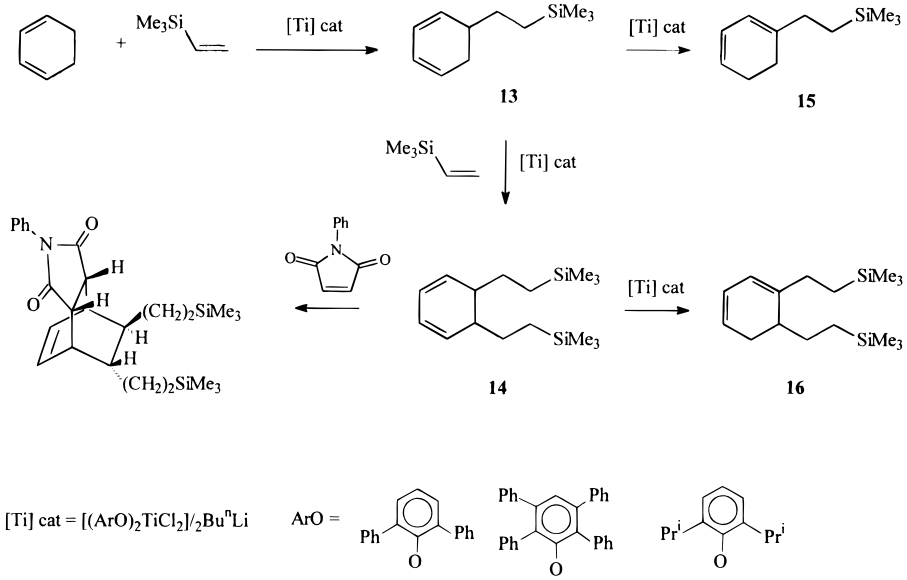


Figure 4. Plot showing the initial appearance with time of **13** when a mixture of 1,3-CHD/$Me_3SiCH{=}CH_2$ (100/250 equiv per Ti) is reacted with **1**−**4**/2Bu^{n}Li in benzene. Reaction mixture: Ti, 0.05 mmol; 1,3-CHD, 5.25 mmol; $Me_3SiCH{=}CH_2$ 13.1 mmol; mesitylene marker, 0.73 mmol; C_6H_6 solvent, total volume 10 mL.

Scheme 5



least substituted olefinic bond of **9** and **10** has been considered. Each of these products can exist as numerous stereoisomers and can undergo subsequent metal-mediated isomerization. Analysis of the reaction mixtures by GC/MS indicates the presence of five distinct isomeric trimers ($C_{18}H_{24}$). To probe the structure of the carbon skeleton of these isomers, a sample of oligomers generated from [**4**/2Bu^{n}Li] was heated with 10%Pd/C to attempt to aromatize the molecules. Analysis of the resulting compounds by GC/MS showed the presence of biphenyl (generated by the dimers) as well as o-triphenyl and p-triphenyl ($C_{18}H_{14}$) as identifiable C_{18}-components. However, dehydrogenation was found to be incomplete with considerable amounts of only partly aromatized products. An alternative strategy involved the hydrogenation of the products using Pt/C under hydrogen. In this case exhaustive hydrogenation occurred yielding isomeric $C_{18}H_{32}$ species. These were identified as *cis*/*trans* isomers of all three di-(cyclohexyl)cyclohexanes. Hence, from these data it appears that this catalyst produces trimeric products containing all three different skeletal fusions (1,2-, 1,3-, and 1,4-). This implies that trimers are produced via both **8** and **9** and possibly also via **10** (Scheme 4).

Cross-Coupling of 1,3-CHD with α-Olefins. The α-olefin $Me_3SiCH{=}CH_2$ undergoes slow dimerization in benzene solution in the presence of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2Cl_2]$/2Bu^{n}Li to produce *trans*-1,3-bis(trimethylsilyl)but-1-ene (identified by ^{1}H and ^{13}C NMR). This catalytic dimerization presumably proceeds via *β*-hydrogen abstraction from a 2,4-bis(trimethylsilyl)-titanacyclopentane intermediate. When an equimolar amount of 1,3-CHD and $Me_3SiCH{=}CH_2$ is mixed in benzene and catalyst added, analysis shows the initial production of the cross-coupled product 5-(*β*-trimethylsilylethyl)-cyclohexa-1,3-diene **13** along with 1,3-CHD dimers. To suppress the 1,3-CHD dimerization, a series of reactions were run with molar excesses of $Me_3SiCH{=}CH_2$ (Scheme 5, Figures 4−6). In Figure 4 is shown the initial

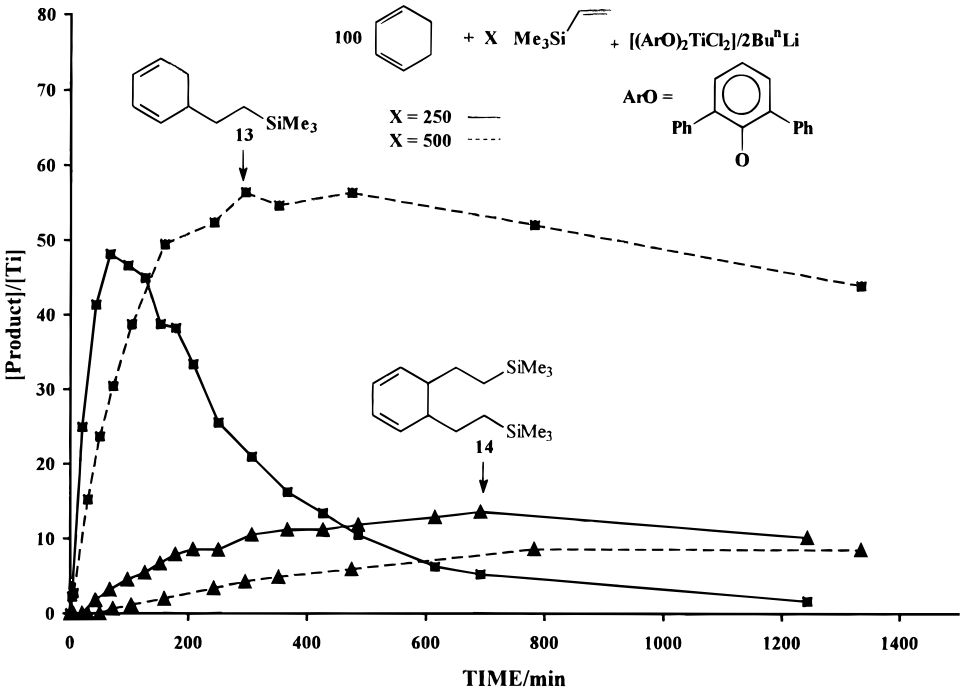


Figure 5. Reaction profile for a mixture of 1,3-CHD/$Me_3SiCH{=}CH_2$ (100/250 equiv per Ti) or (100/500 equiv per Ti) reacted with **1**/2Bu^{n}Li in benzene. Reaction mixture: Ti, 0.05 mmol; 1,3-CHD, 5.25 mmol; $Me_3SiCH{=}CH_2$ 13.1 or 26.2 mmol; mesitylene marker, 0.73 mmol; C_6H_6 solvent, total volume 10 mL.

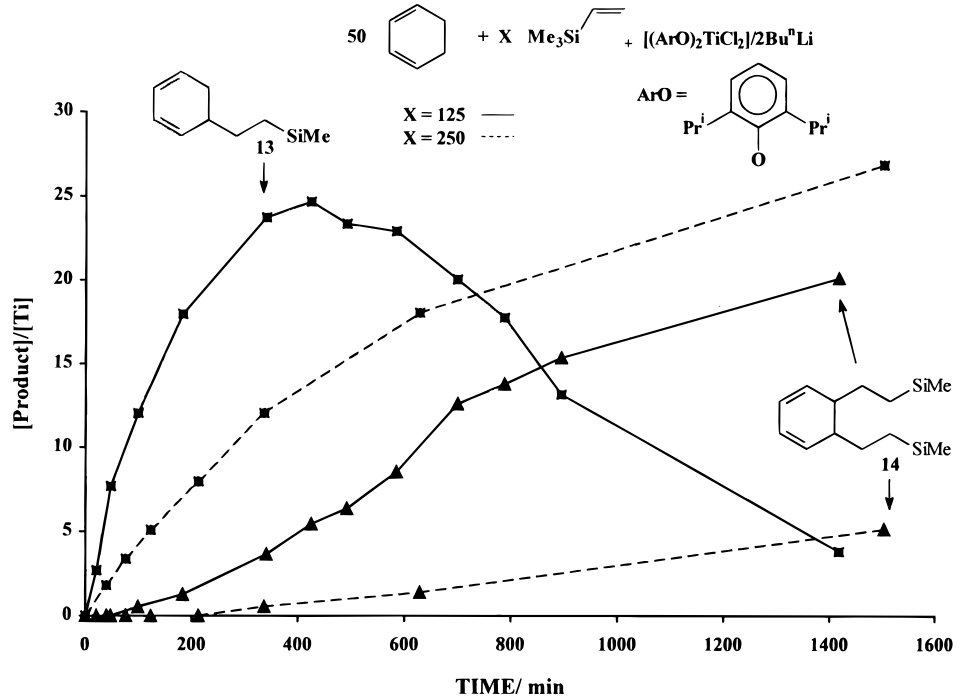
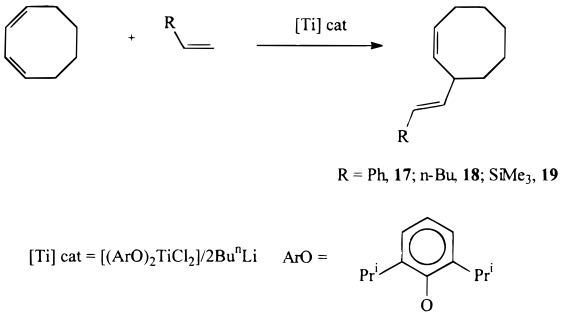


Figure 6. Reaction profile for a mixture of 1,3-CHD/$Me_3SiCH{=}CH_2$ (100/125 equiv per Ti) or (100/250 equiv per Ti) reacted with **4**/2Bu^{n}Li in benzene. Reaction mixture: Ti, 0.11 mmol; 1,3-CHD, 5.25 mmol; $Me_3SiCH{=}CH_2$ 13.1 or 26.2 mmol; mesitylene marker, 0.73 mmol; C_6H_6 solvent, total volume 10 mL.

build up of **13** as a function of time when a mixture of 1,3-CHD/$Me_3SiCH{=}CH_2$ (100/250 equiv per Ti) is reacted with **1**−**4**/2Bu^{n}Li in benzene. It can be seen that the coupling reaction is fastest with the 2,6-diphenylphenoxide precursor (∼1 equiv Ti^{-1} min^{-1}), while the 2,6-di-isopropylphenoxide derived catalyst is on the order of 20 times slower. This reactivity pattern is identical to that seen in the 1,3-CHD dimerization reactions above. The introduction of *meta*-substituents onto the 2,6-diphenylphenoxide nucleus does affect the rate of cross coupling. However, it is difficult to rationalize these differences. Previous work has shown that *meta*-substituents restrict the conformational flexibility of the adjacent *ortho*-phenyl rings leading to effectively bulkier ligands. Hence, the observed differences are probably due to a combination of steric and electronic factors (what aspects of reaction chemistry are not!).

The compound **13** was not the only product observed during these reactions. In Figures 5 and 6 are shown plots of the changes of concentrations of the major components with time

Scheme 6



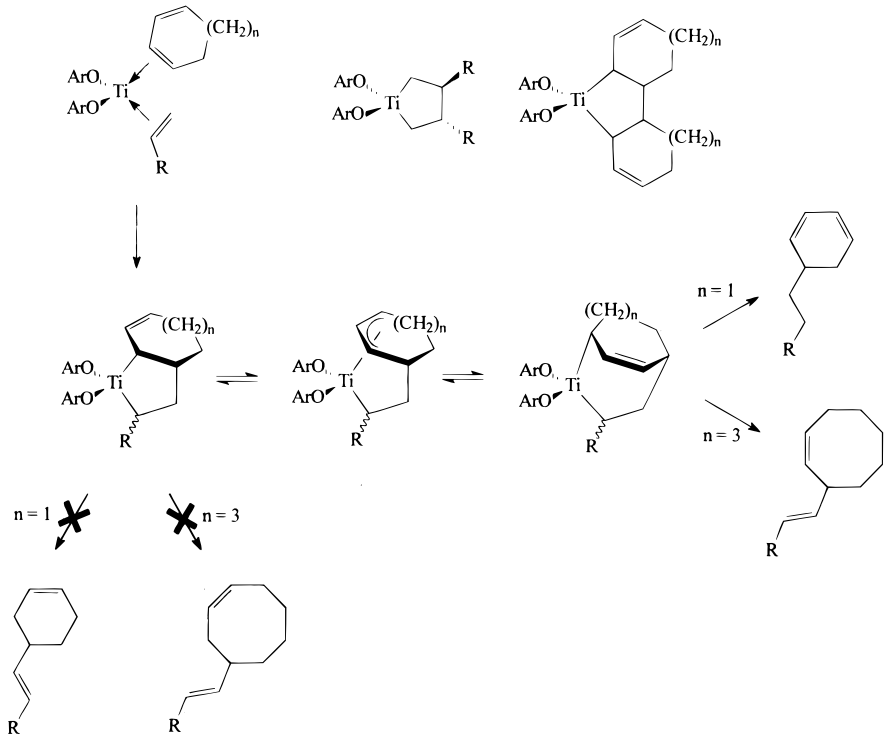
using the catalyst **1**/2Bu^{n}Li and **4**/2Bu^{n}Li with two different ratios of 1,3-CHD/$Me_3SiCH{=}CH_2$. Only one of the other products, *trans*-5,6-bis(*β*-trimethylsilylethyl)cyclohexa-1,3-diene **14** has been fully characterized. In the case of the 2,6-diphenylphenoxide precursor **1** and the 100/250 mixture of 1,3-CHD/$Me_3SiCH{=}CH_2$, the rapid build up of **13** is followed by its slow, almost complete conversion to a mixture of other products. The final major component of the reaction mixture is **14**, while GC/MS data indicates that the other components are isomers of **13** and **14**. On the basis of the work above it seems reasonable to tentatively assign them as 1-(*β*-trimethylsilylethyl)-cyclohexa-1,3-diene **15** and 1,6-bis(*β*-trimethylsilylethyl)cyclohexa-1,3-diene **16** as shown (Scheme 5). When the amount of olefin is increased, it can be seen (Figure 5) first that the buildup of **13** is slowed, and second that subsequent isomerization reactions are also inhibited. These observations are of mechanistic significance (vide infra). In the case of the 2,6-diisopropylphenoxide precursor **4**, the overall reactivity (Figure 6) is slower than with **1**. Again, increasing the olefin to CHD ratio retards the reaction.

Cross-Coupling of 1,3-Cycloocatadiene (1,3-COD) with α-Olefins. In contrast to the above reactivity the dimerization of 1,3-cyclooctadiene (1,3-COD) or the cross coupling of 1,3-COD with α-olefins with most of these catalysts was not observed. However, in one case cross coupling of 1,3-COD with α-olefins was found possible when using the 2,6-diisopropylphenoxide catalyst precursor **4**, although the reactions were very slow compared to the corresponding 1,3-CHD reactions. In this case the products **17**−**19** were identified as not being conjugated dienes but instead 3-vinylcyclooctenes with a *trans* geometry indicated by ^{1}H NMR spectroscopy (Scheme 6).

Mechanism of Cross-Coupling of 1,3-CHD or 1,3-COD with α-Olefins. A mixture of α-olefin and either 1,3-CHD or 1,3-COD with the titanium aryloxides can lead to three different metallacycles as shown (Scheme 7). In the presence of an excess of olefin the titanacyclopentane and cross-coupled metallacycle will dominate. Previous studies have shown that *β*-hydrogen abstraction from five-membered metallacycles is slow in these aryloxide systems.[5] Hence, neither olefin dimerization nor formation of 4-vinyl-cycloolefins is observed. In the case of 1,3-CHD coupled with $Me_3SiCH{=}CH_2$, an allylic shift followed by a *β*-hydrogen abstraction from the initial cyclohexadiene ring leads to the observed product. This is an identical mechanism to the proposed for 1,3-CHD dimerization above. The subsequent coupling of **13** with $Me_3SiCH{=}CH_2$ to product *trans*-**14** requires the exclusive formation of metallacycle **20** (Scheme 8). The *trans* stereochemistry of the product can be rationalized on steric grounds, $Me_3SiCH_2CH_2$ group being *trans* to the metal. However, the final regiochemistry indicates that the coupling initially produces **20** and not **21**. The reason for this is not obvious.

In the case of the coupling of 1,3-COD with α-olefins, analogous intermediates can be formed. In this case, it appears that *β*-hydrogen abstraction occurs from the alkyl tether and not from the original cyclooctadiene ring. The product regiochemistry is, however, consistent with a 1,3-shift to produce a seven-membered titanacycle. The use of styrene-d_8 leads to **17**-d_8 whose ^{1}H NMR spectrum clearly shows the deuterium attached to C8 is cis to the vinyl group (Figure 7). Molecular mechanics calculations show that the vinyl group occupies a pseudoequatorial position. This type of reaction is similar to

Scheme 7



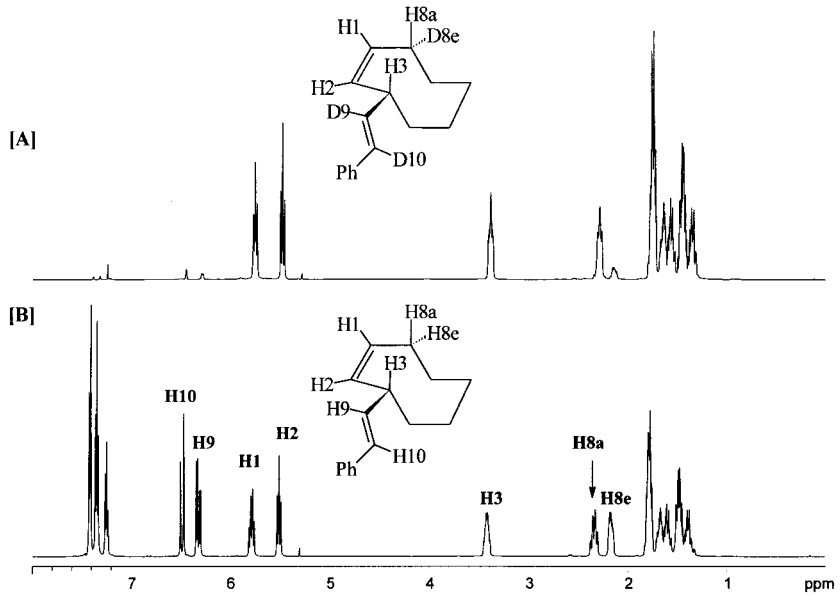
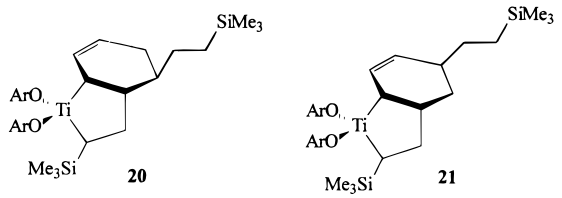


Figure 7. ^{1}H NMR spectra of **17** and **17-*d*$_8$** obtained by coupling 1,3-CHD with styrene or styrene-d_8 using **4**/2Bu^{n}Li as catalyst.

Scheme 8



that observed in the cross coupling of 2,3-dimethylbutadiene with α-olefins. The overall transformation is hence a *cis*-1,4-hydro-vinylation of 1,3-COD. This reactivity is directly related to the selective cross coupling of 1,3-butadienes with α-olefins catalyzed by titanium aryloxide compounds.[17]

Conclusions

The titanium aryloxides used in this study will carry out the non-Diels−Alder dimerization and subsequent oligomerization of 1,3-CHD in hydrocarbon solvents. The initial coupling reaction is rapid and occurs with a high degree of regio- and stereoselectivity. The reaction is argued to occur via *β*-hydrogen abstraction, elimination from seven-membered titanacyclic intermediates. The reactivity can be expanded to include the selective cross coupling of 1,3-CHD and 1,3-COD with α-olefins.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium/benzophenone and stored under dry nitrogen. The ^{1}H and ^{13}C NMR spectra were recorded on Varian Associates Gemini 200 and INOVA 300 MHz spectrometers. Microanalyses were obtained in-house at Purdue University. The phenols used in this study are either commercially available or were obtained by reported methods.[18]

[Ti(OC$_6$HPh$_2$-2,6-Me$_2$-3,5)$_2$Cl$_2$] (3). A sample of 2,6-diphenyl-3,5-methylphenol (10.0 g, 36.5 mmol) was added to a solution containing $TiCl_4$ (1.9 mL, 17.4 mmol) and benzene (40 mL). The resulting red solution was refluxed for 2 h to drive off HCl gas and then slowly allowed to cool affording an orange-red solid. The solvent was decanted away from this solid which was subsequently washed with hexane three times and dried under vacuum affording 9.6 g (90.0%) of **3**. Anal. Calcd for $C_{40}H_{34}Cl_2O_2Ti$: C, 71.98; H, 5.15; Cl, 10.67. Found: C, 71.98; H, 4.89; Cl, 10.89. ^{1}H NMR (C_6D_6, 30 °C): *δ* 2.01 (s, *Me*); 6.74 (s, *para-H*); 7.1−7.3 (aromatics).

[Ti(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_2$] (4). This compound has been previously isolated by a slightly different procedure.[8] Benzene (200 mL) was added to a 1000 mL round-bottom flask under a flow of nitrogen. Liquid $TiCl_4$ (30.5 mL, 0.278 mol) was added via syringe with stirring. Liquid 2,6-diisopropylphenol (99 mL, 100 g, 0.561 mol) was added over 10 min to the solution. The color of the solution became an intense blood red. The benzene was removed in vacuo, and 126.0 g (95.7% yield) of the product as a dark red oil was isolated without further purification. Anal. Calcd for $C_{24}H_{34}Cl_2O_2Ti$: C, 60.90; H, 7.24; Cl, 14.98. Found: C, 64.78; H, 8.80; Cl, 14.31. ^{1}H NMR (C_6D_6, 30 °C): *δ* 1.15 (d, J_{H-H} = 6.87, 12H, CH(C*H*$_3$)$_2$); 3.62 (m, 4H, C*H*(CH$_3$)$_2$); 6.89 (s, 6H, aromatics).

[Ti(OC$_6$H$_3$Me$_2$-2,6)$_2$Cl$_2$] (5). To a yellow solution of [Ti(OC$_6$H$_3$-Me$_2$-2,6)$_4$] **6** (5.25 g, 9.86 mmol) in benzene (30 mL) was added $TiCl_4$ (1.08 mL, 9.86 mmol). The reaction mixture became a deep red color. After 12 h at room temperature, volatiles were removed in vacuo to obtain a red crystalline solid 6.00 g (84%). Anal. Calcd. for $C_{16}H_{18}Cl_2O_2Ti$: C, 52.22; H, 5.02; Cl, 19.64. Found: C, 52.25; H, 5.27; Cl, 19.12. ^{1}H NMR (C_6D_6, 30 °C): *δ* 7.17 (s; aromatics), 2.18 (s; CH_3).

5-(3-Cyclohexenyl)-cyclohexa-1,3-diene (8). To a solution of **4** (50 mg, 0.11 mmol) in benzene (3 mL) was added 1,3-cyclohexadiene (3 mL, 31.4 mmol). A solution of Bu^{n}Li (0.09 mL, 0.21 mmol) in hexane was added while stirring, and the solution changed from a red to a dark burgundy color. After 24 h at room temperature, the reaction was removed from the drybox, hydrolyzed, filtered through a silica column, and concentrated to yield 2.00 g (80%) of **8** as a yellow liquid. ^{1}H NMR (C_6D_6, 30 °C): *δ* 5.87 (m; 2H), 5.60 (m; 4H), 1.21−2.32 (m; 10H). ^{13}C NMR (C_6D_6, 30 °C): *δ* 129.5 (C4), 127.0, 127.1 (C3′, 4′), 126.3 (C1), 124.5, 124.8 (C2, 3), 38.0, 38.2 (C5,1′), 26.1, 26.2, 26.5, 29.2 (C6, 2′, 5′, 6′). EI MS: 160(M$^+$, 12.0%), 145(0.4), 141(0.2), 131-(2.8), 117(4.8), 106(4.0), 91(13.9), 79(100.0), 53(15.6), 51(11.6).

1-(3-Cyclohexenyl)-Cyclohexa-1,3-diene (9) and 2-(3-Cyclohexenyl)-Cyclohexa-1,3-diene (10). To a solution of **4** (50 mg, 0.11 mmol) in benzene (3 mL) was added 1,3-cyclohexadiene (3 mL, 31.4 mmol). A solution of Bu^{n}Li (0.09 mL, 0.21 mmol) in hexane was added while stirring, and the solution changed from a red to a dark burgundy color. After 48 h at room temperature the mixture was hydrolyzed, filtered through a silica column, and purified by TLC to yield 1.50 g (60%) of a yellow oil which consists of a 70/30 mixture of isomers **9** and **10**.

(18) Balaich, G. J.; Hill, J. E.; Waratuke, S. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1995**, *14*, 656.

(19) Vilardo, J. S.; Lockwood, M. A.; Hanson, L. G.; Clark, J. R.; Parkin, B. C.; Fanwick P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1997**, 3353.

Spectroscopic data: **9** ^{1}H NMR (C_6D_6, 30 °C): δ 5.75 (m; 1H), 5.60 (m; 5H), 1.23−2.30 (m; 11H). ^{13}C NMR (C_6D_6, 30 °C): δ 144.2 (C4), 118.2, 124.2, 126.0, 127.0, 127.1 (C1, 2, 3, 3′, 4′), 41.3 (C1′), 23.6, 25.5, 26.0, 27.6, 30.7 (C5, 6, 2′, 5′, 6′). EI MS: 160(M^+, 33.6%), 145(1.2), 141(0.7), 131(6.8), 117(9.4), 106(100.0), 91(85.8), 78(51.4), 53(11.1), 51(13.5). **10** ^{1}H NMR: δ 5.6−5.9 (m; 5H), 1.2−2.3 (m; 11H). ^{13}C NMR: δ = 140.9 (C3), 127.0 (C1, 2, 4, 3′, 4′), 119.3, 124.9, 126.4, 127.0 (C1, 2, 4, 3′, 4′), 40.1 (C1′). EI MS: 160(M^+, 33.7%), 145(5.1), 141(0.9), 131(29.7), 117(26.6), 106(25.9), 91(100.0), 79(50.9), 53(15.3), 51(17.0).

Maleic Anhydride Adduct of 5-(3-Cyclohexenyl)-cyclohexa-1,3-diene (11). To a solution **8** (100 mg, 0.62 mmol) in dichloromethane (3 mL) was added maleic anhydride (80 mg, 0.80 mmol). After 4 h at room temperature, volatiles were removed in vacuo, and the resulting solid was recrystallized from chloroform/pentane to yield white crystals of **11**. ^{1}H NMR ($CDCl_3$, 30 °C): δ 6.33 (t, 7.2 Hz; 1H), 6.20 (t, 7.2 Hz; 1H), 5.65 (m; 2H), 3.32 (m; 1H), 3.21 (m; 1H), 3.09 (m; 1H), 3.12 (m; 1H), 1.0−2.2 (m; 10H). ^{13}C NMR ($CDCl_3$, 30 °C): δ 172.9, 133.5, 131.1, 127.5, 126.0, 45.8, 44.7, 42.1, 39.1, 34.1, 32.7, 30.9, 30.7, 26.7, 25.7. HRMS: Calcd. for $C_{16}H_{18}O_3$: 258.1256, Found 258.1261.

***N*-Phenylmaleimide Adduct of 5-(3-Cyclohexenyl)-cyclohexa-1,3-diene (12).** To a solution of **8** (200 mg, 1.25 mmol) in dichloromethane (3 mL) was added *n*-phenylmaleimide (225 mg, 1.30 mmol). After 24 h at room temperature, volatiles were removed in vacuo and the resulting solid was recrystallized from chloroform/pentane to yield a white microcrystalline solid. ^{1}H NMR ($CDCl_3$, 30 °C): δ 7.1−7.5 (5H), 6.30 (t, 7.1 Hz; 1H), 6.17 (t, 7.1 Hz; 1H), 5.65 (m; 2H), 3.37 (m; 1H), 3.22 (m; 1H), 3.00 (m; 2H), 1.0−2.4 (m; 10H). HRMS: Calcd. for $C_{22}H_{23}NO_2$: 333.1729. Found 333.1712.

5-(*β*-Trimethylsilylethyl)-Cyclohexa-1,3-diene (13). To a solution of **4** (100 mg, 0.22 mmol) in benzene (5 mL) was added 1,3-cyclohexadiene (1.0 mL, 10.5 mmol) and vinyltrimethylsilane (2.00 mL, 12.90 mmol). A solution of Bu^{n}Li (0.17 mL, 0.42 mmol) was slowly added while stirring. The solution changed from a red to a dark burgundy color. The progress of the reaction was monitored by GC. After 5 h at room temperature, the reaction was removed from the drybox, diluted with pentane, and filtered through a silica column. Crude product was purified by TLC to yield 0.87 g (75% based on 1,3-CHD) of a yellow liquid. ^{1}H NMR ($CDCl_3$, 30 °C): δ 5.68−5.92 (m; 1H, 2, 3, 4), 1.26−1.45, 1.97−2.35 (m; 5H, 6, 7), 0.47−0.57 (m; 8H), −0.02 ($SiMe_3$). ^{13}C NMR ($CDCl_3$, 30 °C): δ 131.7 (C4), 126.1 (C2), 124.1 (C1), 123.6 (C3), 35.9 (C5), 28.4, 28.6 (C6,C7), 13.8 (C8), −1.6 ($SiMe_3$). HRMS: Calcd. for $C_{11}H_{20}Si$: 180.1334. Found 180.1332.

***trans*-5,6-Bis(*β*-trimethylsilylethyl)-cyclohexa-1,3-diene (14).** To a solution of **4** (50 mg, 0.11 mmol) in benzene (5 mL) was added 1,3-cyclohexadiene (0.50 mL, 5.25 mmol) and vinyltrimethylsilane (2.00 mL, 12.90 mmol). A solution of Bu^{n}Li (0.09 mL, 0.21 mmol) in hexane was slowly added while stirring. The solution changed from a red to a dark burgundy color. The progress of the reaction was monitored by GC. After 24 h at room temperature, the reaction mixture was removed from the drybox, diluted with pentane, and filtered through a silica column. The crude product was purified by TLC to yield 1.03 g (70% based on 1,3-CHD) of **14** as a yellow liquid. Anal. Calcd. for $C_{16}H_{32}Si_2$: C, 68.49; H, 11.49. Found: C, 68.22; H, 11.70. ^{1}H NMR ($CDCl_3$, 30 °C): δ 5.6−5.9 (m; 1H, 4, 2, 3), 2.05 (m; 5H, 6), 1.25−1.45 (m; C*H*$_2$CH$_2$SiMe$_3$), 0.50 (t, J = 8.7 Hz; C*H*$_2$SiMe$_3$), −0.02 ($SiMe_3$). ^{13}C NMR ($CDCl_3$, 30 °C): δ 130.3 (C1, C4), 122.3 (C2, C3), 40.5 (C5, C6), 29.0 (*C*H$_2$CH$_2$SiMe$_3$), 13.3 (*C*H$_2$SiMe$_3$), −1.3 ($SiMe_3$). HRMS: Calcd. for $C_{16}H_{32}Si_2$: 280.2043. Found 280.2046. Treatment of **14** with maleic anhydride led to the corresponding adduct: ^{1}H NMR (200 MHz, C_6D_6): δ = −0.01, 0.03 (s; $SiMe_3$), 0.4−1.5 (m, C*H*$_2$C*H*$_2$-SiMe$_3$) 2.8−3.3 (m, C*H*), 6.16, 6.37 (t, C*H*=C*H*), 7.2−7.6 (m, aromatic); ^{13}CNMR (75 MHz, $CDCl_3$): δ = −1.5, −1.7 ($SiMe_3$), 14.8, 15.2, 27.2, 30.9, 35.8, 36.7, 39.2, 45.0, 46.8, 48.7, 178.0, 179.5.

***trans*-3-(*β*-Phenylvinyl)-cyclooctene (17).** To a solution of **4** (50 mg, 0.11 mmol) in benzene (5 mL) was added 1,3-cyclooctadiene (0.5 mL, 4.02 mmol) and styrene (1.0 mL, 8.07 mmol). A solution of Bu^{n}Li (0.09 mL, 0.21 mmol) in hexane was slowly added while stirring. The solution changed from a red to a dark burgundy color. The progress of the reaction was monitored by GC. After 72 h at room temperature, the reaction was removed from the drybox, diluted with pentane, and filtered through a silica column. Crude product was purified by TLC to yield 1.26 g (74%) of product as a yellow liquid. ^{1}H NMR ($CDCl_3$, 30 °C): δ 7.34 (d; o−H), 7.27 (t; m−H), 7.18 (t; p−H), 6.41 (d, J = 15.9 Hz; H10), 6.32 (dd, J = 15.9 Hz, 6.8 Hz; H9), 5.74 (q, 8.7 Hz; H1), 5.43 (t, 9.6 Hz; H2), 3.41 (m; H3), 2.34 (m; H8a), 2.18 (m; H8e), 1.3−1.8 (m; 8H). ^{13}CNMR ($CDCl_3$, 30 °C): δ 137.8, 128.4, 126.8, 125.9 (aromatic), 135.1 (C9), 132.6 (C2), 129.3 (C1), 128.4 (C10), 39.3 (C3), 25.6, 26.8, 29.6, 36.5 (C4−7). HRMS: Calcd. for $C_{16}H_{20}$: 212.1565. Found 212.1562.

$C_{16}H_{12}D_8$ (17-*d*$_8$). To a solution of **4** (50 mg, 0.11 mmol) in benzene (5 mL) was added 1,3-cyclooctadiene (0.5 mL, 4.02 mmol) and deuterated styrene (0.92 mL, 8.03 mmol). A solution of Bu^{n}Li (0.09 mL, 0.21 mmol) in hexane was slowly added while stirring. The solution changed from a red to a dark burgundy color. The progress of the reaction was monitored by GC. After 1 week at room temperature, the reaction was removed from the drybox, diluted with pentane, and filtered through a silica column. Crude product was purified by TLC to yield 0.34 g (39%) of product as a yellow liquid. ^{1}H NMR ($CDCl_3$, 30 °C): δ 5.74 (q, 8.7 Hz; H1), 5.43 (t, 9.6 Hz; H2), 3.41 (m; H3), 2.34 (m; H8a), 1.3−1.8 (m; 8H). ^{13}CNMR ($CDCl_3$, 30 °C): δ 137.8, 128.4, 126.8, 125.9 (aromatic), 135.1 (C9), 132.6 (C2), 129.3 (C1), 128.4 (C10), 39.3 (C3), 25.6, 26.8, 29.6, 36.5 (C4−7).

***trans*-3-(*β*-Butylvinyl)-cyclooctene (18).** To a solution of **4** (50 mg, 0.11 mmol) in benzene (5 mL) was added 1,3-cyclooctadiene (0.5 mL, 4.02 mmol) and 1-hexene (1.0 mL, 8.03 mmol). A solution of Bu^{n}Li (0.09 mL, 0.21 mmol) in hexane was slowly added while stirring. The solution changed from a red to a dark burgundy color. The progress of the reaction was monitored by GC. After 1 week at room temperature, the reaction was removed from the drybox, diluted with pentane, and filtered through a silica column. Crude product was purified by TLC to yield 0.35 g (35%) of **18** as a clear liquid. ^{1}H NMR ($CDCl_{36}$, 30 °C): δ 5.64 (m; H1), 5.44 (m; H9, H10), 5.34 (dd, J = 9.3 Hz, 9.8 Hz; H2), 3.13 (m; H3), 2.18 (m; H8a), 0.8−2.1 (m). ^{13}C NMR ($CDCl_3$, 30 °C $_6$): δ 135.0 (C9), 133.8 (C2), 129.2 (C10), 128.9 (C1), 39.2 (C3), 22.4, 25.9, 27.0, 29.9, 32.0, 32.6, 37.1 (C4−7, C11−13), 14.2 (C14).

***trans*-3 (*β*-Trimethylsilylvinyl) Cyclooctene (19).** To a solution of **4** (100 mg, 0.22 mmol) in benzene (5 mL) was added 1,3-cyclooctadiene (1.0 mL, 8.03 mmol) and vinyltrimethylsilane (3.1 mL, 20.08 mmol). Bu^{n}Li (0.17 mL, 0.42 mmol) was slowly added while stirring. The solution changed from a red to a dark burgundy color. The progress of the reaction was monitored by GC. After 48 h at room temperature, the reaction was removed from the oil bath, hydrolyzed with pentane, and filtered through a silica column. Crude product was purified by TLC to yield 1.22 g (73%) of a clear oil. Anal. Calcd. for $C_{13}H_{24}Si$: C, 74.94; H, 11.62. Found: C, 75.14; H, 11.72. ^{1}H NMR ($CDCl_3$, 30 °C): δ 6.05 (dd, 18.6 Hz, 5.8 Hz; H9), 5.68 (m; H1, H10), 5.38 (t, 9.1 Hz; H2), 5.38 (t, 9.1 Hz; H2), 3.19 (m; H3), 2.21 (m; H8a), 2.06 (m; H8e), 1.28−1.71 (m; 8H), 0.05 ($SiMe_3$). ^{13}C NMR ($CDCl_3$, 30 °C): δ 151.2 (C9), 132.9 (C2), 129.5 (C1), 126.0 (C10), 42.5 (C3), 25.9, 27.1, 29.9, 35.3 (C4−7), −1.6 ($SiMe_3$). HRMS: Calcd. for $C_{13}SiH_{24}$: 208.1647. Found 208.1645.

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Supporting Information Available: Description of the experimental procedures for X-ray diffraction studies. Tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and mutiplicities for **5** and **11** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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