# Synthesis and Chemistry of Titanacyclopentane and Titanacyclopropane Rings Supported by Aryloxide Ligation

**Matthew G. Thorn, John E. Hill, Steven A. Waratuke, Eric S. Johnson, Phillip E. Fanwick, and Ian P. Rothwell***

*Contribution from the Department of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, Indiana 47907-1393*

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**Abstract:** Treatment of the titanacyclopentadiene compound [Ti($OC_6H_3Ph_2$-2,6)$_2$($C_4Et_4$)] (**3**) ($OC_6H_3Ph_2$-2,6 = 2,6-diphenylphenoxide) with olefins leads to the formation of a variety of stable titanacyclopentane derivatives along with one equivalent of substituted 1,3-cyclohexadiene. The structural and spectroscopic properties of the ethylene product [Ti($OC_6H_3Ph_2$-2,6)$_2$($CH_2$)$_4$] (**4**) show a ground state titanacyclopentane structure, but facile fragmentation on the NMR time scale to form a bis(ethylene) complex has been detected. The substituted products [Ti($OC_6H_3Ph_2$-2,6)$_2$($C_4H_6R_2$)] (R = Me, **5**; Et, **6**; Ph, **7**) formed from α-olefins RCH=$CH_2$ exist as a mixture of regio- and stereoisomers in hydrocarbon solution. Analysis of a crystal obtained from solutions of **7** showed a *trans*-2,5-diphenyl-titanacyclopentane ring to be present in the solid state. Alternative routes to the titanacyclopentane compounds involve treatment of the dichlorides [Ti($OC_6H_3Ph_2$-2,6)$_2$$Cl_2$] (**1**) or [Ti($OC_6HPh_4$-2,3,5,6)$_2$$Cl_2$] (**2**) with either sodium amalgam (2 Na per Ti) or 2 equiv of $Bu^nLi$ in the presence of the substrate olefin. Using these conditions the titanabicyclic compounds [(ArO)$_2$Ti{$CH_2CH(C_4H_8)CHCH_2$}] (ArO = $OC_6H_3Ph_2$-2,6, **10**; $OC_6HPh_4$-2,3,5,6, **11**) can be obtained by intramolecular coupling of 1,7-octadiene. The spectroscopic properties of **10** and **11** as well as a single-crystal X-ray diffraction analysis of **11** show an exclusive *trans* stereochemistry is present. Thermolysis of **10** or **11** in the presence of excess 1,7-octadiene leads to the catalytic formation of 2-(methylmethylene)cyclohexane (80%) along with *E*,*Z* isomers of 2,6-octadiene (20%). A kinetic study shows the reaction to be zero order in diene with activation parameters, $\Delta H^{\ddagger} = +18.7(5)$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -26(5)$ eu. The diphenyltitanacyclopentane **7** will catalyze the dimerization of styrene to *trans*-1,3-diphenylbut-1-ene followed by isomerization to 1,3-diphenylbut-2-ene. This result shows that although a 2,5-diphenyl regiochemistry was observed in the solid state, styrene dimerization occurs via the 2,4-diphenyltitanacyclopentane intermediate. The facile fragmentation of these titanacyclopentane compounds accounts for the products observed in a number of reactions. Addition of phosphine donor ligands (L) leads to a series of titanacyclopropane compounds [Ti($OC_6H_3Ph_2$-2,6)$_2$($\eta^2$-CHR=$CH_2$)(L)] (R = H, **14**; Me, **15**; Et, **16**; Ph, **17**) along with 1 equiv of olefin. The solid-state structure of the ethylene complex **14** shows the $C_2H_4$ unit lies approximately coplanar with the Ti−$PMe_3$ bond. This structure is not only maintained in solution but slow olefin rotation is observed on the NMR time scale. In the case of the α-olefin products, two isomers are detected by $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy. Addition of $Ph_2C$=O or PhCH=NR (R = Ph, $CH_2Ph$) to the titanacyclopentane and titanacyclopropane compounds leads to different products depending upon the reagent and reaction conditions. These can be classified as 2-oxa(aza)titanacycloheptanes, 2-oxa(aza)titanacyclopentanes, 2,5-dioxa(diaza)titanacyclopentanes, and examples of 2-oxatitanacyclopropane ($\eta^2$-ketone) and 2,7-dioxatitanacycloheptane compounds. The 2-azatitanacyclopentane compounds [Ti($OC_6H_3Ph_2$-2,6)$_2${($PhCH_2$)NCH(Ph)$CH_2CH_2$}] (**30**) and *trans*-[Ti($OC_6H_3Ph_2$-2,6)$_2${(Ph)NCH(Ph)$CH_2$CH(Ph)}] (**31**) react with alkynes to produce the corresponding 2-azatitanacyclopent-4-ene which hydrolyze to produce a stoichiometric equivalent of allylamine. Reaction of **30** with benzonitrile produces the 2,5-diazatitanacyclopent-2-ene [Ti($OC_6H_3Ph_2$-2,6)$_2$(N=CPhCHPhNR)] (**35**) along with ethylene.

## Introduction

The organometallic chemistry of the group 4 metals continues to be dominated by the use of cyclopentadiene ligation.[1] The metallocene dichlorides first discovered by Wilkinson et al.[2] represent an important starting material for a range of stoichiometric and catalytic transformations. A few significant developments have been the utilization of bulky cyclopentadiene ligation,[3] the isolation and study of cationic alkyl derivatives,[4] the chemistry of group 4 metal−ligand multiple bonds,[5,6] and the evolution of chiral metallocenes for carrying out asymmetric synthesis.[7] The success of cyclopentadiene-based group 4 metal chemistry has led a number of research groups to attempt parallel chemistry utilizing "metallocene equivalents".[8] This approach hinges on the much analyzed $\sigma^2,\pi^4$ nature of the interaction of Cp-based ligation with transition metals.[8] The use of isolobal

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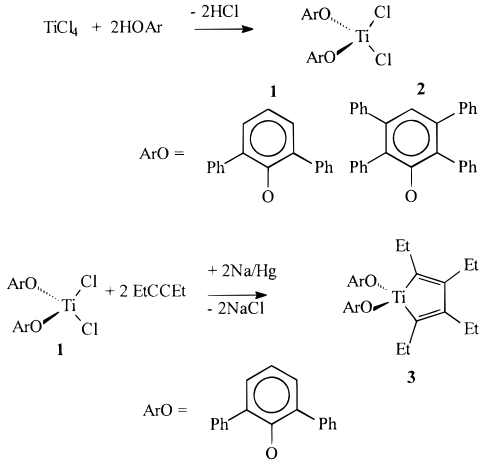
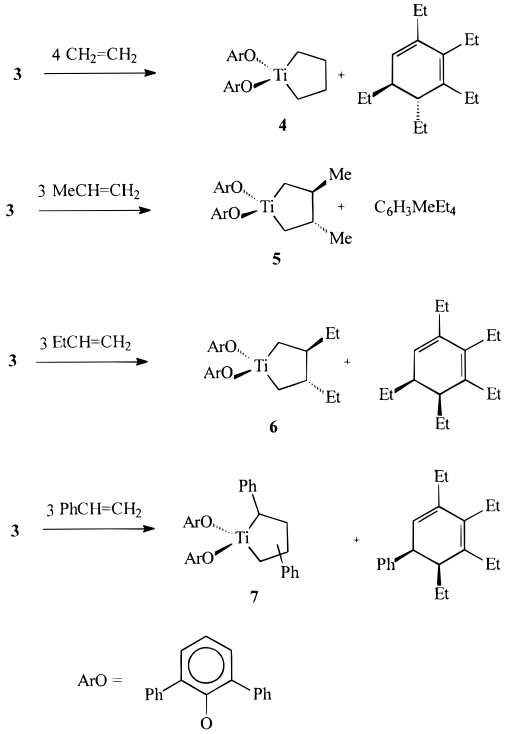
**Scheme 1**



**Scheme 2**



ligands such as the formally dianionic alkylimido group[9] leads to analogous chemistry based upon [Cp(RN)M] (M = group 5) and [$(RN)_2$M] (M = group 6) units.[8]

The alkoxide ligand, whose transition metal chemistry was originally explored by the Bradley and Chisholm groups is a formally monoanionic ligand that can also bond to the metal in a $\sigma^2,\pi^4$ fashion.[10] This analogy was exploited by Wolczanski et al. in employing ligands such as tritox ($Bu^t_3CO$) and silox ($Bu^t_3SiO$) whose cylindrical shape and cone angle mimic that of the cyclopentadiene ligand.[11] Recently Sato et al. have utilized isopropoxide derivatives of titanium as important synthons in organic chemistry.[12] In our group we have focused on sterically demanding, *ortho*-substituted aryloxide ligation to support organometallic chemistry on early d-block metals.[13] In this paper we report on the chemistry of titanacyclic rings supported by aryloxide ligation with emphasis on those derived from olefin substrates. A number of parallels between this aryloxide chemistry and known metallocene chemistry are analyzed. Some aspects of this work have been communicated.[14]

## Results and Discussion

**Synthesis and Characterization of Titanacyclopentane Compounds.** The dichloride compounds [Ti($OC_6H_3Ph_2$-2,6)$_2$-$Cl_2$] (**1**)[15] and [Ti($OC_6HPh_4$-2,3,5,6)$_2Cl_2$] (**2**) can be obtained in high yield by simple treatment of $TiCl_4$ with two equivalents of the parent phenol in hydrocarbon solvents (Scheme 1). Previously we have shown that sodium amalgam reduction of hydrocarbon solutions of **1** in the presence of 3-hexyne leads to the titanacyclopentadiene compound [Ti($OC_6H_3Pr_2$-2,6)$_2$($C_4$-$Et_4$)] (**3**) in high yield (Scheme 1).[16] Solutions of **3** in benzene, react rapidly with excess ethylene, propene, 1-butene, and styrene to produce solutions containing titanacyclopentane derivatives **4**−**7** along with 1 equiv of 1,3-cyclohexadiene (Scheme 2). The regio- and stereochemistry as well as the catalytic formation of the 1,3-cyclohexadiene products is discussed in detail in a subsequent paper.[17] The titanacyclopentane compounds **4**−**6** can be readily isolated pure from these reactions mixtures. A superior synthesis of the diphenyl compound **7** involves sodium amalgam reduction of **1** in benzene solvent in the presence of styrene (Scheme 3). During the course of this reaction an intermediate, intense purple color indicated the formation of the $d^1-d^1$ dimer [Ti($OC_6H_3Ph_2$-2,6)$_2$-($\mu$-Cl)]$_2$ (**8**) which can be isolated pure by simply adding one equivalent of Na/Hg to benzene solutions of **1**. The solid-state structure of **8** has been reported and shows terminal phenoxide ligands and a short Ti-Ti distance of 2.9827(7).[18] Attempts to utilize the 2,3,5,6-tetraphenylphenoxide compound **2** by sodium amalgam reduction in the presence of alkynes or olefins is hampered by the formation of the deep blue, sparingly soluble $d^1-d^1$ compound [Ti($OC_6HPh_4$-2,3,5,6)$_2$($\mu$-Cl)]$_2$ (**9**) (Scheme 3). The low solubility of **9** hinders further reduction to form metallacyclic compounds.

Either by addition of 1,7-octadiene to **3**, or reduction of **1** in the presence of 1,7-octadiene, the titanabicyclic derivative **10** can be isolated. As an alternative to sodium amalgam reduction methods we have also explored the reaction of $Bu^nLi$ with the dichlorides **1** and **2**. The addition of 2 equiv of $Bu^nLi$ to $Cp_2$-$MCl_2$ (the Negishi method)[19] has been utilized to generate a "metallocene equivalent" in the presence of suitable organic substrates. We find that treatment of **1** or **2** with 2 equiv $Bu^n$-

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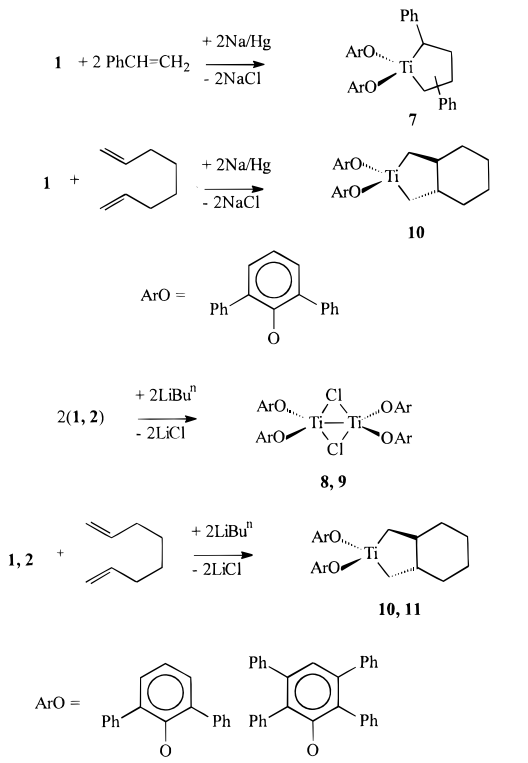
**Scheme 3**




Li in benzene solvent will generate titanacyclopentadiene and titanacyclopentane compounds directly as detected by $^1$H NMR spectroscopy (Scheme 3). In most cases, however, isolated yields were low due to difficulty in separating the products from the reaction mixture. One exception is the treatment of tetraphenylphenoxide **2** with Bu$^n$Li in the presence of 1,7-octadiene. Addition of only 1 equiv of Bu$^n$Li to benzene solutions of **2** lead to formation of deep blue **9**. When 2 equiv of Bu$^n$Li are added with rapid agitation, only a small amount of **9** is produced along with a benzene solution of [Ti(OC$_6$HPh$_4$-2,3,5,6)$_2${CH$_2$CH(C$_4$H$_8$)CHCH$_2$}] (**11**) (Scheme 3). Filtration, removal of solvent, and addition of toluene was found to lead to crystallization of **11** in moderate yield as a toluene solvate.

The solution NMR spectroscopic properties of the titanacyclopentane compounds **4**−**7**, **10**, and **11** are of interest.[20] In the $^{13}$C NMR spectra, signals for the Ti−C(α) and Ti−C($\beta$) carbon atoms display $^1J(^{13}\text{C}-^1\text{H})$ coupling constants close to those expected for sp$^3$-hybridized carbon atoms. Furthermore, the Ti−C(α) chemical shifts are in the range typical for titanium alkyl compounds containing aryloxide ligation. This data supports their proposed structure and is inconsistent with a bis(olefin) formulation for the compounds. There is, however, evidence in the $^1$H NMR spectrum of titanacyclopentane **4** for facile, reversible fragmentation into a "bis(ethylene)" species.[21] In the presence of 1 atm of ethylene, solutions of **4** in C$_6$D$_5$CD$_3$ are stable at temperatures up to 80 °C. At ambient temperatures the α-CH$_2$ and $\beta$-CH$_2$ methylene protons appear as well resolved signals (Figure 1). The excess ethylene appears as a sharp singlet at a chemical shift almost identical for C$_2$H$_4$ simply dissolved in C$_6$D$_5$CD$_3$. Upon raising the temperature

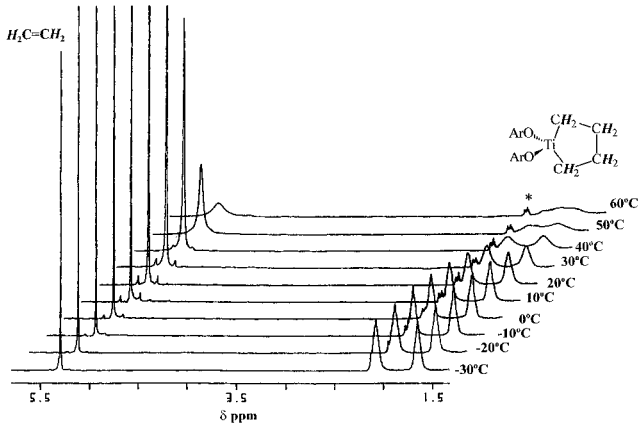
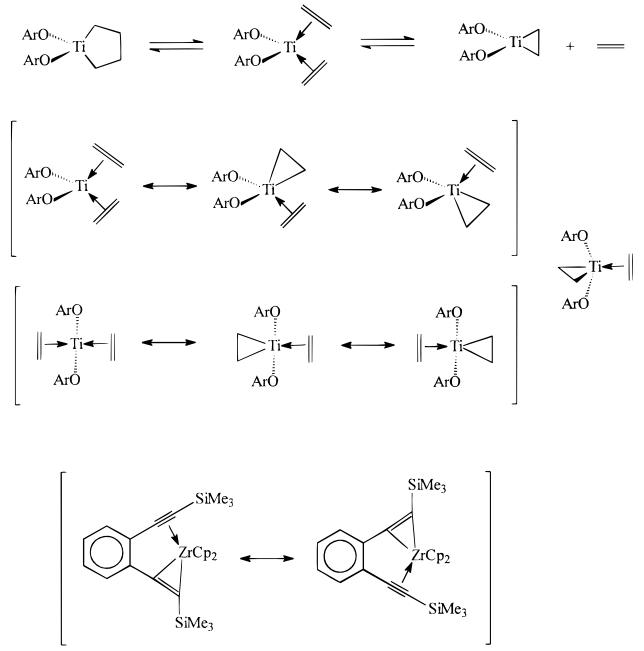



**Figure 1.** $^1$H NMR (200 MHz) spectra of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$)$_4$] (**4**) and ethylene in C$_6$D$_5$CD$_3$ solvent (* indicates protio impurity) over the temperature range −30 to +60 °C.

**Scheme 4**



of the solution, broadening of the methylene proton signals occurs and at +60 °C collapse into the baseline occurs. The signal due to the free ethylene begins to broaden at +40 °C. From the coalescence temperature we estimate the activation energy ($\Delta G^{\ddagger}$) for exchange of the α- and $\beta$-CH$_2$ methylene groups within the titanacyclopentane **4** to be 15.9(5) kcal mol$^{-1}$ at 55 °C. Simulation of the spectra using a program that accommodates a three-site exchange shows that the rate of exchange of methylene groups within **4** (160 s$^{-1}$ at 55 °C) exceeds the rate of exchange of these groups with free ethylene (40 s$^{-1}$ at 55 °C). Accurate simulation of the spectra was not possible due to the variation of the ethylene intensity with temperature (probably reflecting changes in solubility) and the fact that the methylene signals are in reality unresolved multiplets.[22] Furthermore, at temperatures above 60 °C **4** is converted into a new organometallic compound (*vide infra*). We interpret these gross changes as indicating that not only fragmentation of **4** in to a "bis(ethylene)" species occurs (Scheme 4) but that exchange of free and coordinated ethylene also occurs. The most plausible pathway for the intermolecular

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(22) For a discussion of the problems of interpreting NMR exchange rates, see: Green, M. L. H.; Wong, L.-L.; Sella, A. *Organometallics* **1992**, *11*, 2660.

exchange involves a mono(ethylene) intermediate (dissociative exchange, Scheme 4). In the case of the titanium complex [Cp*$_2$Ti($C_2H_4$)], Bercaw et al. have shown that in the presence of ethylene reversible formation of a titanacyclopentane occurs.[23] A much slower rate of rearrangement of a 2,5-dimethylmetallacyclopentane into its 3,4-isomer has been measured by Negishi et al.[24] The exact nature of the intermediate in the rearrangement of **4** is unknown. As shown in Scheme 4 there are a number of geometries ($C_2$ units coplanar, mutually perpendicular, and parallel) and resonance pictures possible. Previous work on a zirconocene system by Buchwald et al. clearly demonstrated the possibility of a delocalized situation best represented as intermediate between two zirconacyclopropene−alkyne complexes (Scheme 4).[25]

In the case of the disubstituted titanacyclopentanes **5**−**7** formed by coupling of α-olefins, there are a total of six possible regio- and stereoisomers. In the case of the dimethyl and diethyl compounds **5** and **6**, $^1$H and $^{13}$C NMR spectra show the presence of a major and a minor isomer. The major isomer in both cases is identified as the *trans*-3,4-disubstituted derivatives. The coupling of α-olefins at group 4 metallocene centers has been investigated by numerous groups. With alkyl substituents a preference for formation of the 3,4-regioisomer has been reported.[26] The presence of a Ti-*CH$_2$* function as well as only one Ti−O−*C* carbon resonance for the aryloxide ligand (i.e., the two aryloxide groups are equivalent) confirms the regio- and stereochemistry of this major isomer.

In the case of the titanabicycles formed by coupling of 1,7-octadiene, a *trans* stereochemistry is again confirmed by the equivalence of the aryloxide ligands in the $^{13}$C NMR spectra as well as by structural and reactivity studies on **11**. The exclusive formation of only the *trans* isomer contrasts with the coupling of 1,7-octadiene at metallocene centers where the kinetically formed *cis* isomer slowly isomerizes to the *trans* form.[20b,27]

The $^1$H NMR spectrum of the titanacyclopentane **7** formed from styrene is broad at ambient temperatures. Furthermore, addition of excess styrene to $C_6D_5CD_3$ solutions of **7** as well as low-temperature NMR studies show that facile metallacycle fragmentation and exchange of free and coordinated styrene is taking place. Presumably the lower barriers to fragmentation/exchange in this case compared to **4** above is a steric consequence of the phenyl substituents. The complexity of the $^1$H NMR spectrum of **7** at low temperatures can only be accounted for by the presence of at least two different substitutional isomers. Based upon structural and reactivity studies we assign these major components as the 2,4- and 2,5-diphenyl derivatives. Studies by Negishi et al. have demonstrated a distinct preference for phenyl substituents to occupy α-positions of metallacyclopentane rings.[28]

The titanacyclopentane compounds **4** and **7** and the titanabicycle derivative **11** have been subjected to single-crystal X-ray diffraction analysis (Figures 2−4 and Tables 1−3). In all cases the formulation of these compounds was confirmed and in the case of **11**, the *trans* stereochemistry was also established

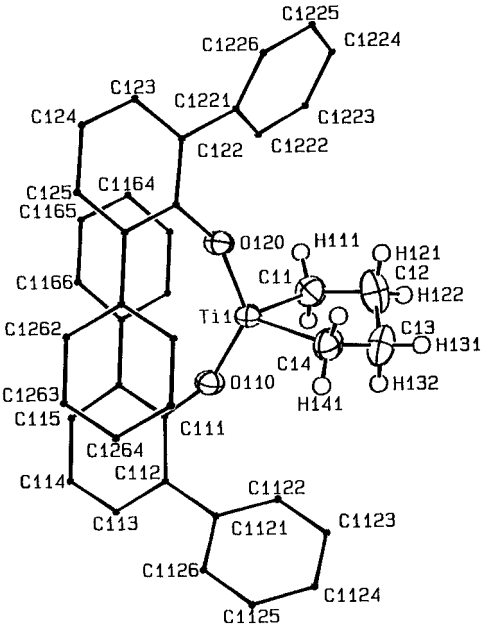


**Figure 2.** Molecular structure of [Ti($OC_6H_3Ph_2$-2,6)$_2$($CH_2$)$_4$] (**4**).

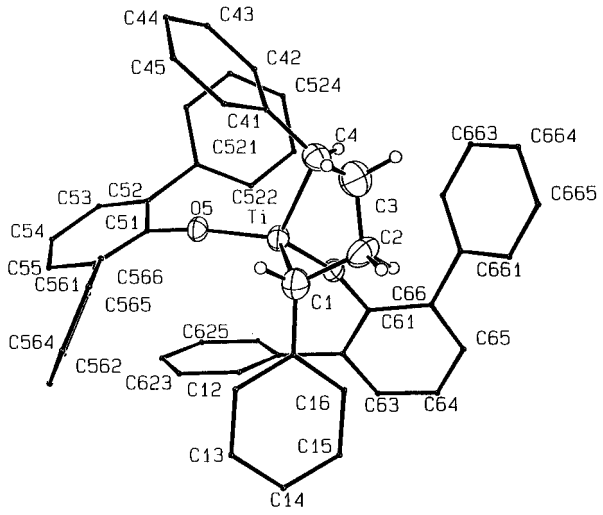


**Figure 3.** Molecular structure of [Ti($OC_6H_3Ph_2$-2,6)$_2${CH(Ph)$CH_2CH_2$-CH(Ph)}] (**7**).

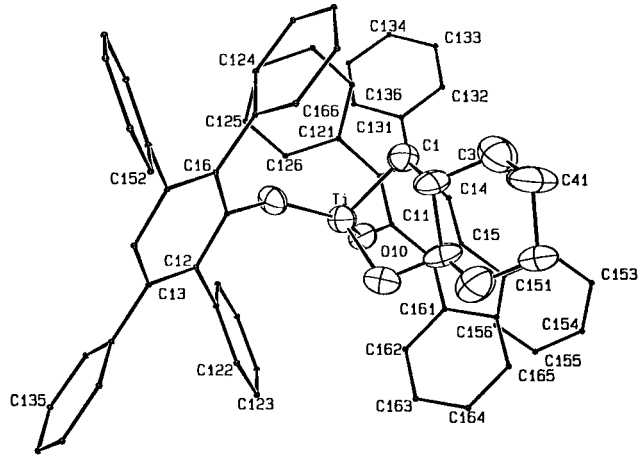


**Figure 4.** Molecular structure of [Ti($OC_6HPh_4$-2,3,5,6)$_2${$CH_2$CH-($C_4H_8$)$CHCH_2$}] (**10**).

(Figure 4). A number of attempts at determining the crystal structure of a sample of **7** were unsuccessful. Eventually a data set was obtained on a crystal which was solved showing the presence of the *trans*-2,5-diphenyl-substituted titanacyclopentane

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**Table 1.** Selected Bond Distances (Å) and Angles (deg) for $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(C_4H_8)]$ (**4**)

| | | | |
|---|---|---|---|
| Molecule 1 | | | |
| Ti(1)−O(110) | 1.799(1) | C(11)−C(12) | 1.510(3) |
| Ti(1)−O(120) | 1.804(1) | C(12)−C(13) | 1.511(4) |
| Ti(1)−C(11) | 2.087(2) | C(13)−C(14) | 1.517(4) |
| Ti(1)−C(14) | 2.084(2) | | |
| O(110)−Ti(1)−O(120) | 132.62(6) | Ti(1)−C(11)−C(12) | 106.6(1) |
| O(110)−Ti(1)−C(11) | 104.96(7) | Ti(1)−C(14)−C(13) | 106.3(1) |
| O(110)−Ti(1)−C(14) | 108.12(7) | C(11)−C(12)−C(13) | 109.4(2) |
| C(11)−Ti−C(14) | 85.59(9) | C(12)−C(13)−C(14) | 109.8(2) |
| Ti(1)−O(110)−C(111) | 157.9(1) | Ti(1)−O(120)−C(121) | 155.7(1) |
| Molecule 2 | | | |
| Ti(2)−O(210) | 1.802(1) | C(21)−C(22) | 1.520(3) |
| Ti(2)−O(220) | 1.817(1) | C(22)−C(23) | 1.512(4) |
| Ti(2)−C(21) | 2.084(2) | C(23)−C(24) | 1.512(4) |
| Ti(2)−C(24) | 2.084(2) | | |
| O(210)−Ti(2)−O(220) | 135.05(6) | Ti(2)−C(21)−C(22) | 106.1(1) |
| O(210)−Ti(2)−C(21) | 107.84(7) | Ti(2)−C(24)−C(23) | 105.4(1) |
| O(210)−Ti(2)−C(24) | 104.23(7) | C(21)−C(22)−C(23) | 109.8(2) |
| C(21)−Ti−C(24) | 86.22(8) | C(22)−C(23)−C(24) | 109.6(2) |
| Ti(2)−O(210)−C(211) | 159.1(1) | Ti(2)−O(220)−C(221) | 151.3(1) |

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\{CH(Ph)CH_2CH_2CH(Ph)\}]$ (**7**)

| | | | |
|---|---|---|---|
| Ti−O(5) | 1.801(3) | Ti−O(6) | 1.804(3) |
| T−C(1) | 2.103(6) | Ti−C(4) | 2.115(5) |
| C(1)−C(2) | 1.537(7) | C(2)−C(3) | 1.516(8) |
| C(3)−C(4) | 1.546(8) | | |
| O(5)−Ti−O(6) | 126.1(1) | C(1)−Ti−C(4) | 85.6(2) |
| Ti−C(1)−C(2) | 97.7(4) | Ti−C(4)−C(3) | 105.6(4) |
| C(1)−C(2)−C(3) | 110.0(5) | C(2)−C(3)−C(4) | 111.6(5) |
| Ti−O(5)−C(51) | 157.4(3) | Ti−O(6)−C(61) | 161.1(3) |

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for $[Ti(OC_6HPh_4\text{-}2,3,5,6)_2\{CH_2CH(C_4H_8)CHCH_2\}]$ (**11**)

| | | | |
|---|---|---|---|
| Ti−O(10) | 1.802(3) | Ti−C(1) | 2.061(5) |
| C(1)−C(21) | 1.49(2) | C(21)−C(21) | 1.65(3) |
| O(10)−Ti−O(10) | 135.0(2) | O(10)−Ti−C(1) | 106.6(2) |
| O(10)−Ti−C(1)' | 105.2(2) | C(1)−Ti−C(1) | 88.5(3) |
| Ti−O(10)−C(11) | 149.4(3) | Ti−C(1)−C(21) | 105.0(8) |
| C(1)−C(21)−C(21) | 106.5(8) | | |

ring (Figure 3). In all three titanacyclopentane derivatives the Ti−O and Ti−C distances are within the ranges typical of aryloxide and alkyl groups bound to 4-coordinate Ti(IV).[29]

The titanacyclopentane compounds **4**−**7** react with excess $H_2O$ to produce a mixture of organic products along with 2 equiv of phenol (Scheme 5). For the unsubstituted derivative **4**, butane was detected along with significant amounts of ethylene and ethane (GC analysis and $^1H$ NMR). In the case of the diphenyl derivative **7** an almost quantitative conversion to a 50/50 mixture of styrene and ethylbenzene was observed. It, therefore, appears that water acts as a simple Lewis donor ligand as well as a protic source and induces the fragmentation of the titanacyclopentane prior to protonation of the bound olefin (Scheme 5). Hydrolysis of titanabicycle **10** and **11** yields *trans*-1,2-dimethylcyclohexane.

During an attempt to obtain crystals of the dimethyltitanacyclopentane complex **5** by slow cooling of a hexane solution, the accidental introduction of trace amounts of moisture led to the formation of crystals of an oxo complex **12** (Scheme 5). The molecular structure of **12** (Figure 5, Table 4) shows that it has originated by reactions of 2 equiv of **5** with 1 equiv of water. A similar type of reaction occurs between metallocene dialkyls and traces of water.[30] The protonation of one of the Ti−C bonds

(29) Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1990**, *29*, 3221.

(30) Hunter, W. E.; Nrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

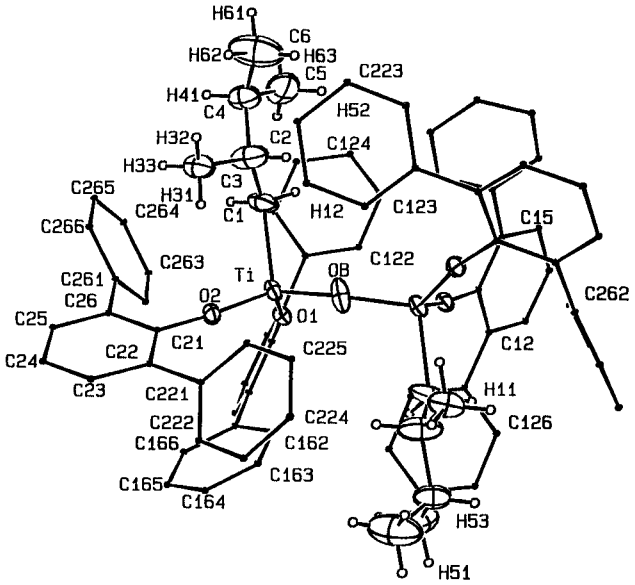



**Figure 5.** Molecular structure of $[\{Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2\text{-}CHMeCMe_2)\}_2(\mu\text{-}O)]$ (**12**).

**Scheme 5**

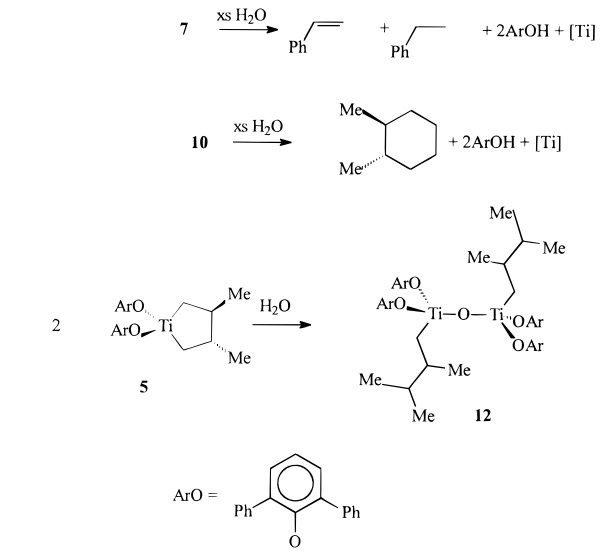



**Table 4.** Selected Bond Distances (Å) and Angles (deg) for $[\{Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2CHMeCHMe_2)\}_2(\mu\text{-}O)]$ (**12**)

| | | | |
|---|---|---|---|
| Ti−O(1) | 1.793(3) | Ti−O(2) | 1.795(2) |
| Ti−O(B) | 1.801(1) | Ti−C(1) | 2.087(5) |
| O(1)−Ti−O(2) | 119.4(1) | O(1)−Ti−O(B) | 110.2(1) |
| O(1)−Ti−C(1) | 100.0(2) | O(2)−Ti−O(B) | 113.46(9) |
| O(2)−Ti−C(1) | 107.2(2) | O(B)−Ti−C(1) | 104.5(2) |
| Ti−O(B)−Ti | 152.3(1) | Ti−O(1)−C(11) | 160.7(2) |
| Ti−O(2)−C(21) | 167.6(3) | Ti−C(1)−C(2) | 129.7(5) |

in **5** leads to an alkyl group which gives insight into the regiochemistry of the original titanacyclopentane ring. Clearly the alkyl group in **12** can only be formed from the 3,4-dimethyltitanacyclopentane ring, although the same group can be formed from either the *cis* or *trans* stereoisomers.

**Thermal Stability of Titanacyclopentanes: Catalytic Cyclization of 1,7-Octadiene and Dimerization of Styrene.** When a solution of titanacyclopentane **7** in $C_6H_6$ is heated at 100 °C in the presence of excess styrene, catalytic dimerization occurs to initially produce *trans*-1,3-diphenylbut-1-ene (Scheme 6).[31] This product presumably arises via a 2,4-diphenyltitanacyclopentane intermediate by abstraction of a hydrogen from the 3-position of the ring. The *trans*-1,3-diphenylbut-1-ene is

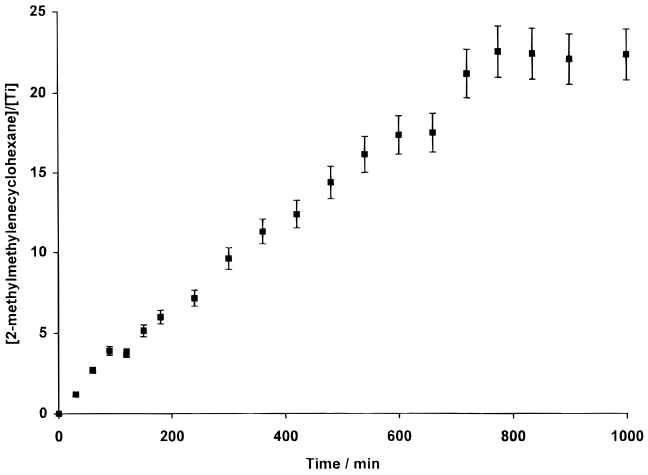
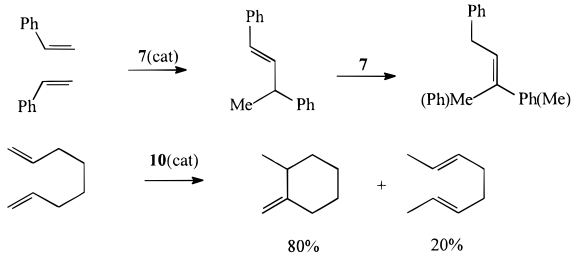



**Figure 6.** Plot showing the appearance with time of 2-(methylmethylene)cyclohexane within a $C_6D_6$ solution containing [Ti($OC_6H_3Ph_2$-2,6)$_2${$CH_2CH(C_4H_8)CHCH_2$}] (**10**, 0.0345 mmol) and 1,7-octadiene (0.977 mmol) heated at 118 °C.

**Scheme 6**




subsequently isomerized within the reaction mixture to produce 1,3-diphenylbut-2-ene. This result shows that although structural studies demonstrate the presence of the *trans*-2,5-diphenyl derivative in the solid state, thermal reactivity in solution proceeds via the 2,4-diphenyl isomer.

Titanabicycle **10** catalytically converts 1,7-octadiene into a mixture of 2-methyl-methylenecyclohexane[31−34] (80% by GC) and 2,6-octadiene (predominantly E,E by $^{13}C$ NMR,[35] Scheme 6). Previous work by Nakamura et al. has shown that low valent titanocene systems are excellent catalysts for the internalization of terminal olefins and nonconjugated dienes.[35] Recent work by Negishi et al. has shown a zirconocene isomerization of α,ω-dienes to produce metal bound 1,3-diene structures.[36] Attempts to use **10** as a catalyst for the cyclization of 1,6-heptadiene and 1,8-nonadiene led mainly to olefin isomerization. A kinetic study of the cyclization of 1,7-octadiene showed the reaction to be zero order in [diene]. The catalyst **10** was observed (NMR) to be the predominant Ti species in solution (as long as there is excess 1,7-octadiene present) and remains active for a significant number of turnovers (Figure 6, Table 5). Activation parameters were obtained for the formation of 2-(methylmethylene)cyclohexane over a 40° temperature range (Figure 7).

**Table 5.** First-Order Rate Constants for the Cyclization of 1,7-Octadiene Catalyzed by **10**

| *T*, C | $10^3k$, $s^{-1}$ | equiv of $Ti^{-1}$ $h^{-1}$ |
|---|---|---|
| 94 | 0.102 | 0.366 |
| 108 | 0.217 | 0.78 |
| 118 | 0.487 | 1.75 |
| 134 | 1.28 | 4.60 |

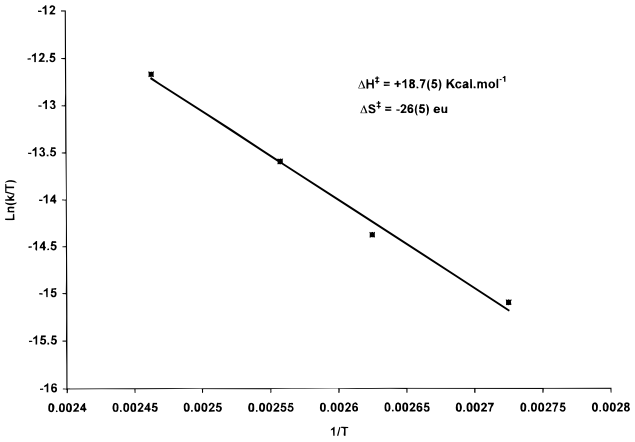
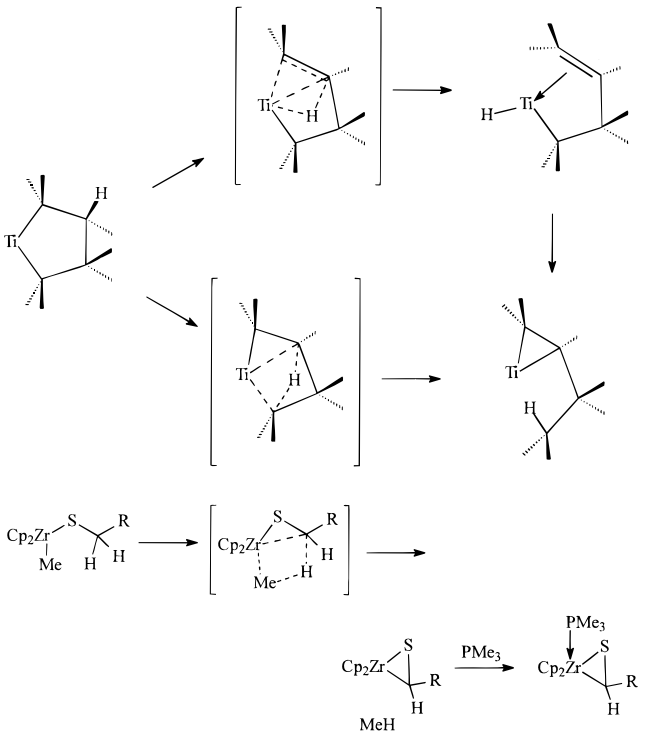



**Figure 7.** Plot of ln ($k/T$) vs $1/T$ for the cyclization of 1,7-octadiene into 2-(methylmethylene)cyclohexane (data in Table 5).

**Scheme 7**




A number of distinct mechanistic pathways for these olefin dimerization/cyclization reactions can be envisaged proceeding via the titanacyclopentane intermediate. The two most reasonable differ as to whether the $\beta$-hydrogen abstraction occurs initially by the metal center to generate an intermediate hydride or in a concerted fashion by the adjacent α-carbon center (Scheme 7). This latter process corresponds to an intramolecular $\sigma$-bond metathesis reaction, a pathway that is common for ligand cyclometallation at $d^0$ metal centers.[37] These reactions are directly related to the breakdown of compounds such as [$Cp_2$M-

(31) Dimerization of olefins and cyclization of α,ω-dienes via metallacyclopentanes, see: (a) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *101*, 4558. (b) Smith, G.; Mclain, S. J.; Schrock, R. R. *J. Organomet. Chem.* **1980**, *202*, 269.

(32) Linear dimerization of dienes, see: Christoffers, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6422 and references therein.

(33) For an *alternative* selective cyclization of α,ω-dienes catalyzed by scandium hydrides, see: Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, *74*.

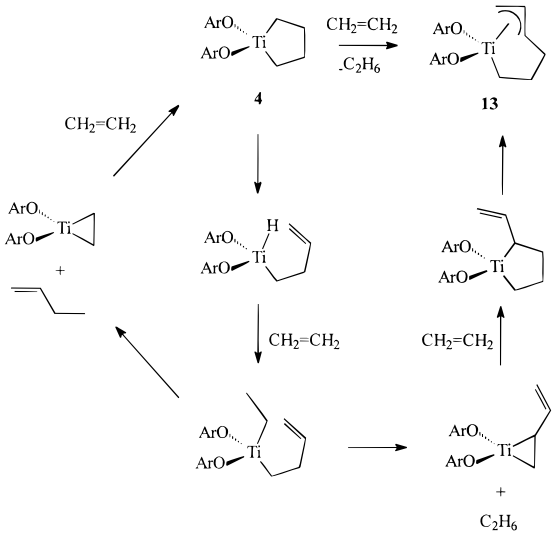
(34) For references to the ring closing metathesis of α,ω-dienes, see: Zuercher, W. J.; Hashimoto, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 6634 and references therein.

(35) Akita, M.; Yasuda, H.; Nagasuna, K.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 554.

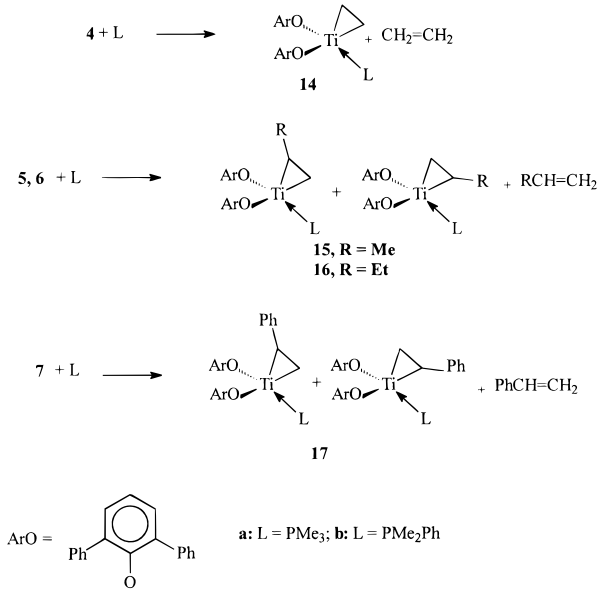
(36) Negishi, E.; Maye, J. P.; Choueiry, D. *Tetrahedron* **1995**, *51*, 4447.

(37) Rothwell, I. P. In *Selective Hydrocarbon Activation*; Davis, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds; VCH Publishers: New York, 1990; pp 43−75.

**Scheme 8**




**Scheme 9**




(X)(R)] (M = Zr, Hf) in which the X group contains at least one $\beta$-CH bond. Mechanistic studies by Buchwald et al. on the formation of thioaldehyde complexes led to the conclusion that the reactions proceed via a concerted pathway (Scheme 7).[38] Particularly informative were a large negative entropy of activation and a primary deuterium kinetic isotope effect. A substituent effect study yielded a Hammet plot with $\rho = +0.39$, indicating positive charge build up on the hydrogen being transferred in the transition state.[38]

The kinetic study of the cyclization of 1,7-octadiene yielded a value of $\Delta S^{\ddagger} = -26(5)$ eu (Figure 7), consistent with the highly ordered transition state required in the concerted pathway. However, when an equimolar mixture of $C_6H_5CH{=}CH_2$ and $C_6D_5CD{=}CD_2$ was heated with titanacyclopentane **7** at 100 °C in $C_6D_6$, scrambling of both $\alpha$- and $\beta$-olefinic H/D atoms was observed ($^1$H and $^{13}$C NMR) at a rate much faster than dimerization. The catalyst for this exchange process is presumably a titanium hydride species which undergoes reversible insertion of styrene monomers to produce both $\alpha$- and $\beta$-phenethyl groups. It is possible that solutions of **7** contain such a hydride species as a contaminant. An alternative explanation is that the scrambling is catalyzed by the hydride generated by $\beta$-hydrogen abstraction by the metal center. If this was indeed the case it would imply that this species was sufficiently long-lived to carry out multiple insertions with free styrene.

The thermal instability of **4** is also mechanistically significant. When solutions of **4** and excess ethylene in $C_6D_6$ are heated at 80 °C, almost quantitative conversion to the titanacycloheptene complex **13** occurs (Scheme 8). This complex has been previously isolated by addition of 1,3-butadiene to **4**.[39] Small amounts of 1-butene and ethane were also present in solution ($^1$H NMR). The thermal decompostion of metallacyclopentanes of the group 4 metals has been studied by many researchers dating back to the pioneering studies of Whitesides et al.[40] This reactivity parallels exactly that reported by Erker et al. for the zirconacyclopentane [$Cp_2Zr(CH_2)_4$], where ethylene dimerization was curtailed by formation of a zirconacycloheptene complex.[41] The ethylene complex [$Cp^*_2Ti(C_2H_4)$] was demonstrated by Cohen and Bercaw to be a catalyst for the conversion of ethylene to 1,3-butadiene and ethane.[23] These reactions are believed to proceed via intermediates formed by $\beta$-hydrogen abstraction by the metal center. The resulting 3-butenyl hydride can then insert an extra equivalent of ethylene and eliminate ethane with formation of a 1,3-butadiene complex which in the case of **4** would produce **13** (Scheme 8). An alternative pathway proposed by Erker et al. proceeds via a titanium dihydride intermediate.[41]

The above observations, therefore, imply that the catalytic dimerization of styrene by **7** and cyclization of 1,7-octadiene by **10** proceed via metal hydride intermediates and not by way of a concerted pathway. The zero-order dependence on olefin is consistent with either rate-determining $\beta$-hydrogen abstraction and relatively fast subsequent steps or alternatively reversible $\beta$-hydrogen with a rate determining elimination step. This latter scenario could not, however, involve olefin in the rate-determining step. A pathway which is consistent with these mechanistic findings and avoids the intermediacy of a highly unsaturated species [$Ti(OAr)_2$] is shown for ethylene in Scheme 8. Rate-determining $\beta$-hydrogen abstraction is followed by insertion of an equivalent of olefin to generate a dialkyl intermediate. In the case of ethylene, ethane elimination eventually leads to **13**, whereas in the case of styrene and 1,7-octadiene elimination of product generates a monoolefin species which can rapidly regenerate a titanacylopentane (Scheme 8).

**Synthesis and Characterization of Titanacyclopropane Compounds.** The titanacyclopentane compounds **4**−**7** react rapidly in $C_6D_6$ solution with either $PMe_3$ or $PMe_2Ph$ to produce deep-purple solutions containing 1 equiv of olefin and new organometallic compounds. These new compounds are formulated as titanacyclopropane (monolefin) species containing a single phosphine ligand (Scheme 9). In the case of the propene-, butene- and styrene-derived complexes, a mixture of two isomers is observed in solution by $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy. The presence of two, nonequivalent Ti−C resonances in the $^{13}$C NMR spectrum of the ethylene complex (**14**) indicates a structure for the molecule in which the C−C unit is coplanar, as opposed to perpendicular, to the Ti−P bond. This situation was confirmed by a single-crystal X-ray diffraction analysis of **14a** (Figure 8, Table 6). The two isomers present for **15**−**17** are due to the olefin substituents being positioned either proximal or distal to the phosphine ligand. This reactivity, the structures of compounds **15**−**17** as well as the

(38) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3175.
(39) Balaich, G. J.; Hill, J. E.; Waratuke, S. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1995**, *14*, 656.
(40) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.
(41) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 914.

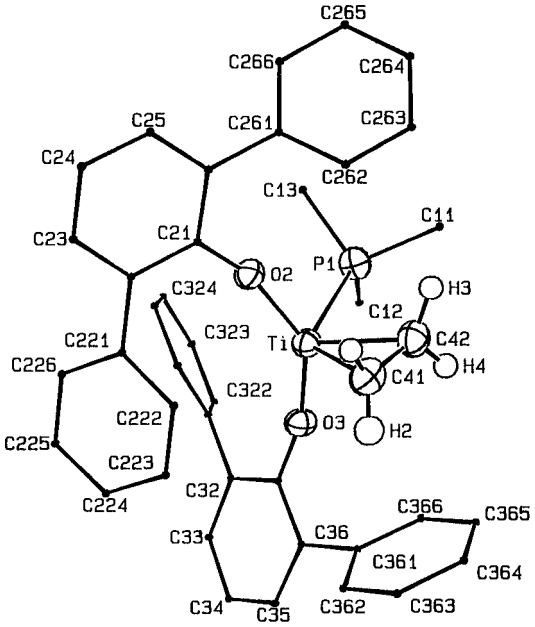



**Figure 8.** Molecular structure of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2CH_2)(PMe_3)]$ (**14a**).

**Table 6.** Selected Bond Distances (Å) and Angles (deg) for $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(\eta^2\text{-}CH_2CH_2)(PMe_3)]$ (**14a**)

| | | | |
|---|---|---|---|
| Ti−P(1) | 2.5633(5) | Ti−O(2) | 1.835(1) |
| Ti−O(3) | 1.838(1) | Ti−C(41) | 2.110(2) |
| Ti−C(42) | 2.148(2) | C(41)−C(42) | 1.425(3) |
| P(1)−Ti−O(2) | 93.39(4) | P(1)−Ti−O(3) | 98.39(4) |
| P(1)−Ti−C(41) | 122.67(5) | P(1)−Ti−C(42) | 83.97(5) |
| O(2)−Ti−O(3) | 140.73(5) | O(2)−Ti−C(41) | 100.76(7) |
| O(2)−Ti−C(42) | 100.76(7) | O(3)−Ti−C(41) | 103.86(7) |
| O(3)−Ti−C(42) | 107.33(7) | C(41)−Ti−C(42) | 39.09(7) |
| Ti−O(2)−C(21) | 160.9(1) | Ti−O(3)−C(31) | 161.3(1) |

**Table 7.** Structural Parameters for Selected Group 4 Metalacyclopropane Compounds

| compound | M−C, (Å) | C−C, (Å) | ref |
|---|---|---|---|
| $H_2C{=}CH_2$ | | 1.337(2) | |
| $[Cp^*_2Ti(CH_2CH_2)]$ | 2.160(4) | 1.438(5) | 22 |
| $[(ArO)_2Ti(CH_2CH_2)(PMe_3)]$ (**14a**) | 2.110(2)<br>2.148(2) | 1.425(3) | *a* |
| $[Cp_2Zr(CH_2CH_2)(PMe_3)]$ | 2.354(3)<br>2.332(4) | 1.449(6) | 42 |
| $[Cp_2Zr(CH_2CHPh)(PMe_3)]$ | 2.35(1)<br>2.35(2) | 1.46(2) | 42 |
| $[Cp_2Hf(CH_2CMe_2)(PMe_3)]$ | 2.316(8)<br>2.368(9) | 1.46(10 | 43b |
| $[\{(Et_3P)_2Cl_3Zr\}(CH_2CH_2)\{(Et_3P)_2Cl_3Zr\}]$ | 2.42(2)<br>2.44(2) | 1.69(3) | 44 |

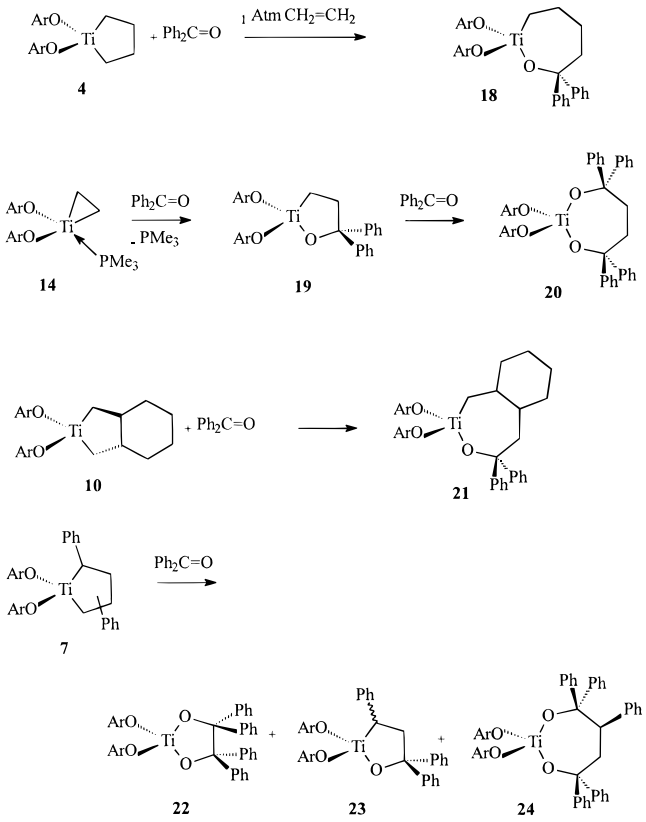
[a] This work.

lack of facile olefin rotation is similar to that reported for group 4 analogous containing cyclopentadiene ligation.[28,42−44]

The most interesting feature of the solid-state structure of **14** pertains to the structural parameters of the titanacyclopropane ring. In Table 7 are collected selected parameters of related molecules for comparison.

It can be seen that although there is a pronounced elongation of the ethylene C−C bond upon coordination to the titanium center in **14a**, the lengthening is slightly less than found in corresponding mononuclear metallocene derivatives of Ti, Zr, and Hf (Table 7). The bonding of the ethylene moiety in the species $[Cl_2Ti(CH_2CH_2)]$ has been theoretically analyzed.[46]

**Scheme 10**




**Synthesis and Characterization of Oxa- and Azatitanacyclic Compounds.** We have probed the reactivity of the isolated titanacyclopentane and titanacyclopropane species toward ketones and imine reagents. Initially focusing upon the reaction with benzophenone, $Ph_2C{=}O$, by varying the reaction conditions we have been able to isolate and characterize oxatitanacyclopropane, -pentane, and -heptane as well as dioxatitanacyclopentane and -heptane species. The titanacyclopentane **4** will react with $Ph_2C{=}O$ in the presence of excess ethylene to produce the oxatitanacycloheptane complex **18**. In the absence of excess ethylene in solution, **4** produces a mixture of not only **18** but also oxatitanacyclopentane **19** and dioxatitanacycloheptane **20** (Scheme 10). These latter two compounds are also synthesized by addition of 1 or 2 equiv of $Ph_2C{=}O$ to $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(\eta^2\text{-}CH_2{=}CH_2)(PMe_3)]$ **14** (Scheme 10). Cohen and Bercaw demonstrated the clean coupling of $\eta^2$-bound ethylene with acetaldehyde to produce an oxatitanacyclopentane ring.[23] Some related reactions include coupling of $\eta^2$-cyclobutene with acetone[44a] and the intramolecular coupling of ene−one substrates.[47] In contrast, addition of $Ph_2C{=}O$ to the titanabicycle **10** was found to produce the oxatitanacycloheptane **21** along with small amounts of the dioxatitanacyclopentane (benzopinacolate) **22**. The addition of $Ph_2C{=}O$ to the diphenyltitanacyclopentane **7** is found, even in the presence of excess styrene, to yield a mixture of oxatitanacyclopentane **23**, dioxatitanacycloheptane **24**, and dioxatitanacyclopentane **22**. In

(42) (a) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761.

(43) Binger, P.; Muller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Kruger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035.

(44) (a) Fisher, R. A.; Buchwald, S. L. *Organometallics* **1990**, *9*, 871. (b) Buchwald, S. L.; Kreutzer, K. A.; Fisher, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4600.

(45) Cotton, F. A.; Kibala, P. A. *Polyhedron* **1987**, *6*, 645.

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(47) (a) Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 3182. (b) Hewlett, D. F.; Whitby, R. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1684.

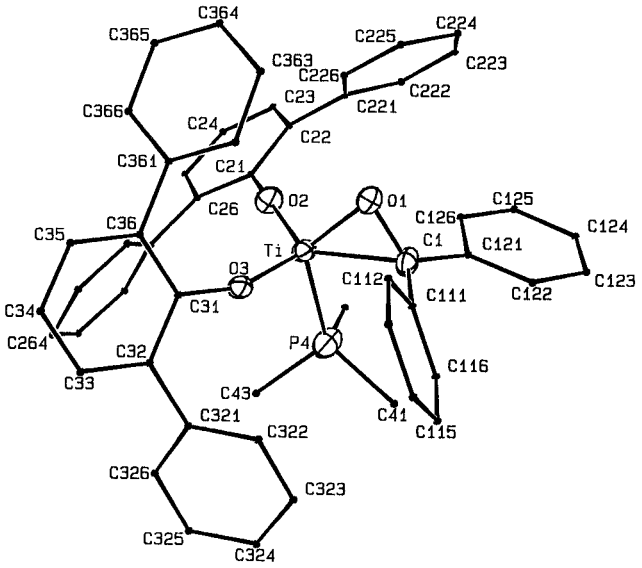



**Figure 9.** Molecular structure of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(OCPh_2)(PMe_3)]$ (**25**).

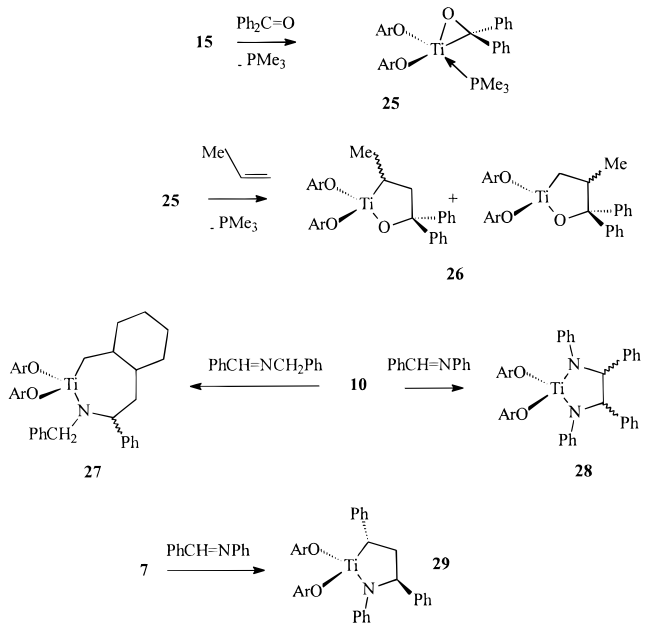
**Table 8.** Selected Bond Distances (Å) and Angles (deg) for $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(\eta^2\text{-}OCPh_2)(PMe_3)]$ (**25**)

| | | | |
|---|---|---|---|
| Ti−P(4) | 2.592(3) | Ti−O(1) | 1.849(5) |
| Ti−O(2) | 1.839(5) | Ti−O(3) | 1.817(4) |
| Ti−C(1) | 2.150(7) | C(1)−O(3) | 1.397(8) |
| P(4)−Ti−O(1) | 127.0(2) | P(4)−Ti−O(2) | 88.6(2) |
| P(4)−Ti−O(3) | 105.5(2) | P(4)−Ti−C(1) | 90.9(2) |
| O(1)−Ti−O(2) | 110.1(2) | O(1)−Ti−O(3) | 109.0(2) |
| O(1)−Ti−C(1) | 40.0(2) | O(2)−Ti−O(3) | 115.8(2) |
| O(2)−Ti−C(1) | 133.0(3) | O(3)−Ti−C(1) | 109.5(2) |
| Ti−O(2)−C(21) | 167.8(5) | Ti−O(3)−C(31) | 159.2(4) |

product **23**, NMR spectroscopy shows that the ketone has coupled with the methylene carbon of the styrene ligand, leading to the 3,3,5-triphenyl-2-oxa-titanacyclopentane regioisomer. This reaction has also been interrogated utilizing labeled $Ph_2{}^{13}C{=}O$, allowing not only confirmation of the $^{13}C$ NMR chemical shifts of the carbon, but also to confirm that the reagent benzophenone is incorporated into only the three products shown (Scheme 10).

The addition of $Ph_2C{=}O$ to the propene complex **15** followed by vacuum removal of volatile products, allows the isolation of the oxatitanacyclopropane ($\eta^2$-ketone) complex **25** (Scheme 11). If the propene is not removed, or if excess propene is added to a solution of **25**, the oxatitanacyclopentane **26** is produced along with free $PMe_3$. The $\eta^2$-ketone complex **25** has been subjected to single crystal X-ray diffraction analysis (Figure 9, Table 8). Although a large number of aldehyde and ketone derivatives of the group 4 metals are known, they are typically bimolecular with bridging ketonic functions.[48] There are, however, mononuclear ketene species which are directly related to **25**.[49] The structural parameters for **25** are interesting, showing a distinct elongation of the C−O bond, 1.397(8), compared to a value of 1.23 in $Ph_2C{=}O$.[50] The Ti−O(3) distance of 1.817(4) is slightly shorter than the distances to the aryloxide oxygen atoms. These parameters indicate strong $\pi$-back-bonding into the $\pi^*$ (C═O) orbital, and strongly support the oxatitanacyclopropane resonance picture.

**Scheme 11**




Related reactivity is observed in the reactions involving the imine reagents PhCH═NR (R = Ph, $CH_2Ph$). The titanabicycle **10** produces the azatitanacycloheptane **27** (R = $CH_2Ph$, stereochemistry undetermined), whereas benzylideneaniline was observed to produce 1,7-octadiene and a new species believed to be diazatitanacyclopentane **28** (Scheme 11) based upon spectroscopic data. The diphenyltitanacyclopentane **7** reacts with PhCH═NPh to produce the azatitanacyclopentane **29** in high yield. Analysis of the $^1H$ NMR spectrum of **29** as well as the labeled compound obtained using $Ph^{13}CH{=}NPh$, shows a *trans* 2,3,5-triphenyl isomer to be present. We justify the single regio- and stereochemistry for **29** on steric grounds. The *trans* stereochemistry allows the phenyl rings at the C-3 and C-5 positions to occupy pseudoaxial and pseudoequatorial positions respectively (Scheme 11). The axial positioning at C-3 removes conflict with the N-*Ph* group while the preference for an equatorial site for the phenyl group at C-5 will help avoid clashes with the bulky 2,6-diphenylphenoxide ligands which lie above and below the plane of the azatitanacyclopentane.

Reaction of the ethylene derivative **14** with $PhCH{=}NCH_2$-Ph produces the azatitanacyclopentane **30** and 1 equiv of $PMe_3$ (Scheme 12). In contrast the propene complex forms the diazatitanacyclopentane **31** along with propene. The $^{13}C$ NMR spectrum of **31** shows only one Ti−O−*C*(aryloxide) resonance consistent with a *trans* stereochemistry as shown (Scheme 12). The azatitanacyclopentanes **29** and **30** react with alkynes to displace olefin and generate azatitanacyclopent-4-enes (Scheme 12). The regiochemistry of these organometallic products is readily confirmed by NMR methods and hydrolysis is found to produce the corresponding allylic amines (Scheme 13). The regio- and stereochemistry of the coupling of alkynes and imines at zirconocene metal centers has been extensively investigated by Buchwald et al.[51] The displacement of ethylene from zirconacyclopentene rings has been shown to be a synthetically useful reaction.[52]

(48) (a) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (b) Kropp, K.; Skibbe, V.; Erker, G.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353. (c) Erker, G.; Hoffmann, U.; Zwetler, R.; Betz, P.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 630. (d) Erker, G.; Czisch, P.; Schlund, R.; Angermund, K.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 364. (e) Stella, S.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1053. (f) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668. (g) Fachinetti, G.; Biran, C.; Floriani, C.; Villa, A. C.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995.

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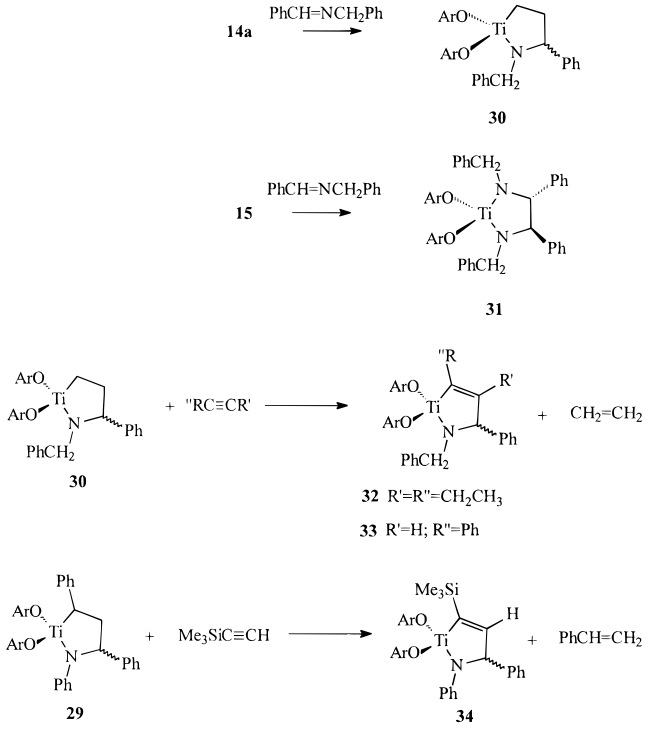
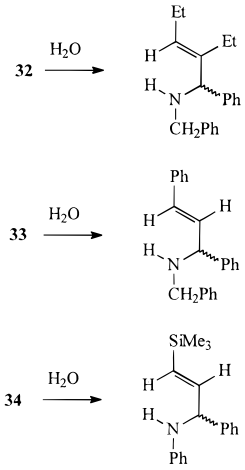
(50) Fleischer, E. B.; Sung, N.; Hawkinson, S. *J. Phys. Chem.* **1968**, *72*, 4311.

(51) (a) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (b) Buchwald, S. L.; Wannamaker, M. W.; Watson, B. T. *J. Am. Chem. Soc.* **1989**, *111*, 776.

**Scheme 12**




**Scheme 13**




The azatitanacyclopentane compound **30** reacts with one equivalent of benzonitrile to produce one equivalent of ethylene and a new titanium compound **35** (Scheme 14). The new compound is formulated as a 2,5-diazatitanacylopent-2-ene derivative on the basis of spectroscopic data and a single crystal diffraction study of **35** (Figure 10, Table 9). The molecular structure of **35** shows a planar metallacycle ring, in contrast to the nonplanar situation found for 2,5-diazatitanacylopent-3-ene species. Solutions of **35** were found to be converted over days into 2,5-diazatitanacylopent-3-ene (ene-diamide) **36**, which was obtained as an impure liquid, but found to crystallize as its pyridine adduct **37** (Scheme 14). The isomerization of 2-aza-metallacyclopentene rings has literature precedence.[23,53]

## Conclusions

Good synthetic routes to a variety of titanacyclopentane and titanacyclopropane species for use in organometallic synthesis have been developed. The use of sterically demanding aryloxide groups has been found to generate chemistry which is both different and complimentary to that developed with cyclopentadiene ligation. The solution spectroscopic properties and reactivity of the titanacyclopentane rings can only be accounted for by facile fragmentation into a bis(olefin) intermediate. The synthetic utility of both types of metallacycles has been probed with ketones and imines and shown to lead to a wide variety of new oxa and aza-titanacycles.

(52) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687.

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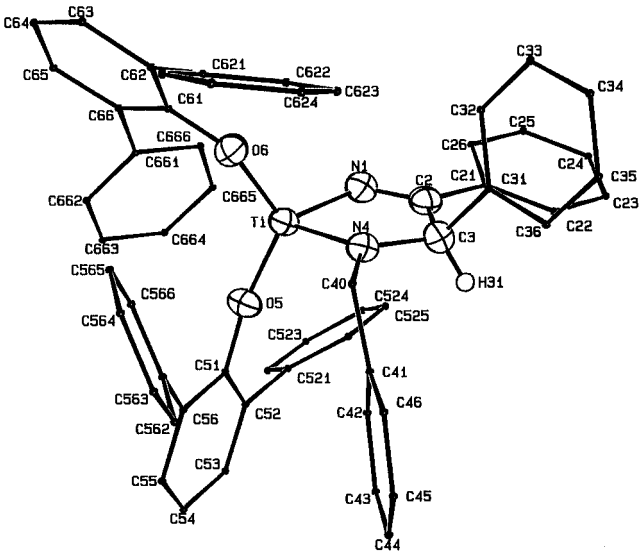


**Figure 10.** Molecular structure of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\{NCPhCHPhN(CH_2Ph)\}]$ (**35**).

**Scheme 14**

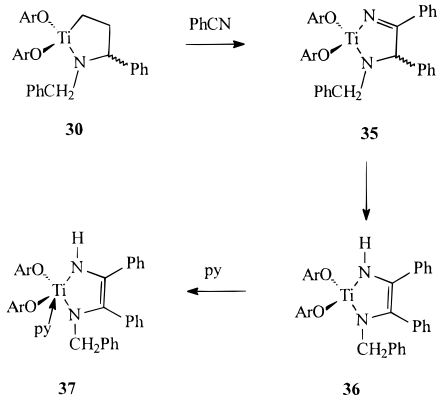


**Table 9.** Selected Bond Distances (Å) and Angles (deg) for $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\{NCPhCHPhN(CH_2Ph)\}]$ (**35**)

| | | | |
|---|---|---|---|
| Ti−O(5) | 1.816(2) | Ti−N(4) | 1.886(2) |
| Ti−O(6) | 1.829(2) | Ti−N(1) | 1.910(2) |
| N(1)−C(2) | 1.277(3) | C(2)−C(3) | 1.529(4) |
| N(4)−C(3) | 1.466(3) | | |
| O(5)−Ti−O(6) | 124.10(8) | O(5)−Ti−N(1) | 113.61(9) |
| O(5)−Ti−N(4) | 108.71(9) | O(6)−Ti−N(1) | 114.72(9) |
| O(6)−Ti−N(4) | 104.27(9) | N(4)−Ti−N(1) | 81.9(1) |
| Ti−O(5)−C(51) | 161.5(2) | Ti−O(6)−C(61) | 151.5(2) |

## Experimental Section

All manipulations were carried out under $N_2$ using a Vacuum Atmospheres dry box and conventional Schlenk techniques. All solvents were dried by distillation over sodium/benzophenone under a nitrogen atmosphere. $^1H$ and $^{13}C$ NMR spectra were recorded using a Varian Gemini 200 MHz instrument. Microanalytical, mass spectral, and X-ray crystallographic data were acquired through Purdue in-house facilities. The compounds $[Ti(OC_6H_3Ph_2\text{-}2,6)_2Cl_2]$ (**1**)[15] and $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(C_4Et_4)]$ (**3**)[16] were obtained by published procedures. Synthetic details can be found in the Supporting Information.

**[Ti(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_2$] (2).** Anal. Calcd for $TiO_2Cl_2C_{66}H_{48}$, **2**·$C_6H_6$: C, 79.92; H, 4.88; Cl, 7.15. Found: C, 79.97; H, 4.70; Cl, 7.21. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.50−7.50 (aromatics).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$)$_4$] (4).** Anal. Calcd for $TiC_{40}H_{34}O_2$: C, 80.80; H, 5.76. Found: C, 80.69; H, 6.02. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.90−7.41 (aromatics); 1.98 (broad), 1.60 (broad, C$H_2$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 160.3 (Ti−O−*C*); 89.7 [$^1J$($^{13}$C−$^1$H) = 127.4 Hz, Ti*C*H$_2$]; 31.1 [$^1$J($^{13}$C−$^1$H) = 127.7Hz, TiCH$_2$*C*H$_2$].

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$CHMeCHMeCH$_2$)] (5).** Anal. Calcd for $TiC_{42}H_{30}O_2$: C, 81.02; H, 6.15. Found: C, 81.31; H, 6.56. $^1$H NMR ($C_6D_6$, 30 °C): *trans* isomer $\delta$ 6.88−7.48 (aromatic); 2.04 (m, C*H*Me); 1.88 (t, 10.6 Hz), 1.24 (dd, TiC*H*$_2$, 10.6 Hz, 4.1 Hz); 0.93 (d, CH*Me*, 5.4 Hz). $^{13}$C NMR ($C_6D_6$, 30 °C): *trans* isomer $\delta$ 160.1 (Ti−O−*C*); 98.0 [$^1J$($^{13}$C−$^1$H) = 129.2 Hz, Ti*C*H$_2$]; 44.8 [$^1J$($^{13}$C−$^1$H) = 126.2 Hz, *C*HMe]; 23.3 (CH*Me*).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$CHEtCHEtCH$_2$)] (6).** Anal. Calcd for $TiC_{44}H_{42}O_2$: C, 81.22; H, 6.51. Found: C, 81.54; H, 6.91. $^1$H NMR ($C_6D_6$, 30 °C): *trans* isomer $\delta$ 6.88−7.8 (aromatics); 2.03 (m, C*H*Et); 1.85 (t), 1.22 (m, Ti*CH*$_2$); 1.22 (m, C*H*$_2$CH$_3$); 0.60 (t, CH$_2$C*H*$_3$). $^{13}$C NMR ($C_6D_6$, 30 °C): *trans* isomer $\delta$ 160.2 (Ti−O−C); 95.0 [$^1J$($^{13}$C−$^1$H) = 126.5 Hz, Ti*C*H$_2$]; 48.7 [$^1J$($^{13}$C−$^1$H) = 126.8 Hz, *C*HEt]; 28.9 (*C*H$_2$CH$_3$); 18.1 (CH$_2$*C*H$_3$)

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${C$_4$H$_6$(Ph)$_2$}] (7).** Anal. Calcd for $TiC_{52}H_{42}O_2$: C, 83.57; H, 5.64. Found: C, 83.63; H, 5.67. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.20−7.41 (aromatics); 3.30 (m), 2.77 (broad m), 2.00 (broad m), 1.30 (m). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 160.3 (Ti−O−C); 107.0 (broad, Ti*C*HPh).

**Dimerization of Styrene Catalyzed by [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${C$_4$H$_6$(Ph)$_2$}] (7).** In a typical procedure 0.10 g (0.15 mmol) of [Ti(OC$_6$H$_3$-Ph$_2$-2,6)$_2$Cl$_2$] **(1)** was dissolved in 5 mL of benzene. To this solution was added 2.1 equiv of Bu$^n$Li (0.12 mL, 0.31 mmol) and 25 equiv of styrene (0.42 mL, 3.64 mmol). This reacton mixture was then heated at approximately 100 °C initially producing *trans*-1,3-diphenylbut-1-ene. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.80−7.40 (aromatics); 6.33 [AB, $^3J$($^1$H−$^1$H) = 16.0 Hz, *trans* C*H*═C*H*]; 3.42 (m, C*H*PhCH$_3$); 1.33 (d, C*H*$_3$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$135.1, 128.4 (*C*HPh═*C*H); 42.5 (*C*HPhCH$_3$); 21.2 (*C*H$_3$). HRMS: calcd for $C_{16}H_{16}$ 208.1252, found 208.1251. Upon further heating this initial product was isomerized to 1,3-diphenylbut-2-ene. $^1$H NMR ($C_6D_6$, 30 °C): 6.80−7.40 (aromatics); 5.89 [t, $^3J$($^1$H−$^1$H) = 7.3 Hz, C*H*]; 3.30 (d, C*H*$_2$Ph); 1.86 (s, C*H*$_3$).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$($\mu$-Cl)]$_2$ (8).** Anal. Calcd for $Ti_2C_{72}H_{52}O_4Cl_2$: C, 75.34; H, 4.57; Cl, 6.18. Found: C, 81.54; H, 4.85; Cl, 6.29. The X-ray crystal structure of **8** has been previously published.

**[Ti(OC$_6$HPh$_4$-2,3,5,6)$_2$($\mu$-Cl)]$_2$ (9).** Anal. Calcd for $TiO_4Cl_2C_{120}H_{84}$: C, 82.05; H, 4.82; Cl, 4.09. Found: C, 81.75; H, 5.05; Cl, 4.12.

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${CH$_2$CH(C$_4$H$_8$)CHCH$_2$}] (10).** Anal. Calcd for $TiC_{44}H_{40}O_2$: C, 81.47; H, 6.22. Found: C, 81.56; H, 6.41. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.90−7.42 (aromatics); 0.4−2.0 (aliphatics). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 160.2 (Ti−O−C); 95.9 [$^1J$($^{13}$C−$^1$H) = 128.0 Hz, Ti*C*H$_2$]; 46.8 [$^1J$($^{13}$C−$^1$H) = 129.0 Hz, TiCH$_2$*C*H]; 37.7 [$^1J$($^{13}$C−$^1$H) = 124.5 Hz, TiCH$_2$CH*C*H$_2$]; 27.0 [$^1J$($^{13}$C−$^1$H) = 124.5 Hz, TiCH$_2$CHCH$_2$*C*H$_2$]. The product of hydrolysis of **10** was identified as *trans*-1,2-dimethylcyclohexane by comparison of the $^1$H NMR spectrum and GC trace to that of an authentic sample.

**[Ti(OC$_6$HPh$_4$-2,3,5,6)$_2${CH$_2$CH(C$_4$H$_8$)CHCH$_2$}] (11).** To a stirred mixture of [Ti(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_2$] (**2**, 3.00 g, 3.03 mmol) and 1,7-octadiene (0.90 mL, 6.06 mmol, two fold excess) in benzene (10 mL) was slowly added Bu$^n$Li (6.06 mmol) in hexane (2.5 M solution). The resulting brown suspension was filtered and the solvent removed under vacuum. The oily residue was dissolved in a minimum of toluene and allowed to stand whereupon orange crystals of the toluene solvate **3b**·-2$C_7H_8$ were deposited. The yield of **3b** obtained in this fashion has been found to vary from 15−75%. Satisfactory microanalytical data on **3b** could not be obtained presumably due to loss of toluene solvate.

**[{Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$CHMeCMe$_2$)}$_2$($\mu$-O)] (12).** Anal. Calcd for $Ti_2C_{84}H_{66}O_3$: C, 79.99; H, 6.07. Found: C, 80.35; H, 6.58. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.83−7.39 (aromatics); 0.42−1.48 (aliphatics). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 160.7 (Ti−O−C); 99.6, 99.2 (Ti*C*H$_2$); 42.4, 41.8 (*C*HMe); 35.9, 35.7 (*C*HMe$_2$); 20.6, 20.5 (CH*Me*); 17.8, 17.5, 17.5, 17.3 (CH*Me*$_2$).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$CH$_2$)(PMe$_3$)] (14a).** Anal. Calcd for $TiC_{41}H_{39}O_2P$: C, 76.63; H, 6.12; P, 4.82. Found: C, 76.99; H, 6.14; P, 4.58. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.87−7.36 (aromatics); 1.72 [td, $^3J$($^1$H−$^{31}$P) = 6.8 Hz, $^3J$($^1$H−$^1$H) = 12 Hz C$H_2$ adjacent to PMe$_3$]; 0.51 [t, $^3J$($^1$H−$^{31}$P) < 1 Hz, C$H_2$ away from PMe$_3$]; 0.22 (d, PMe$_3$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 160.0 (Ti−O−C); 78.0 [d, $^1J$($^{13}$C−$^1$H) = 147.6 Hz, $^2J$($^{13}$C−$^{31}$P) = 5.9 Hz, *C*H$_2$ adjacent to PMe$_3$]; 67.0 [$^1J$($^{13}$C−$^1$H) = 149.6 Hz, *C*H$_2$ away from PMe$_3$], 12.5 (d, P*Me*$_3$). $^{31}$P NMR ($C_6D_6$, 30 °C): $\delta$ 2.43 (*P*Me$_3$).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$CH$_2$)(PMe$_2$Ph)] (14b).** $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.80−7.27 (aromatics); 1.70 (m), 0.5 (m, C$H_2$C$H_2$); 0.45 (d, P*Me*$_2$Ph). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 160.0 (Ti−O−C); 79.4 [d, $^2J$($^{13}$C−$^{31}$P) = 2.8 Hz, *C*H$_2$ adjacent to PMe$_2$Ph]; 68.8 (*C*H$_2$ away from PMe$_2$Ph); 11.0 (d, P*Me*$_2$Ph).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$CHMe)(PMe$_3$)] (15a).** Anal. Calcd for $TiC_{42}H_{41}O_2P$: C, 76.82; H, 6.29; P, 4.72. Found: C, 76.83; H, 6.46; P, 4.98. $^1$H NMR ($C_6D_6$, 30 °C): major isomer $\delta$ 6.8−7.6 (aromatics); 1.61 (m), 1.48 (m, C$H_2$); 1.43 (d, 8.0 Hz, CH*Me*); 0.53 (m, C*H*Me); 0.14 (d, P*Me*$_3$); minor isomer $\delta$ 2.32 (m, C*H*Me); 1.04 (d, 8.0 Hz, CH*Me*); 0.90 (m), 0.44 (m, C$H_2$); 0.02 (d, P*Me*$_3$). $^{31}$C NMR ($C_6D_6$, 30 °C) major isomer $\delta$ 80.7 [d, $^1J$($^{13}$C−$^1$H) = 148.1 Hz, $^2J$($^{13}$C−$^{31}$P) = 5.5 Hz, *C*H$_2$]; 76.2 [$^1J$($^{13}$C−$^1$H = 148.1 Hz, *C*HMe]; 22.6 (CH*Me*); 12.5 (P*Me*$_3$); minor isomer $\delta$ 89.2 [d, $^1J$($^{13}$C−$^1$H) = 148.3 Hz, $^2J$($^{13}$C−$^{31}$P) = 6.4 Hz, *C*HMe]; 74.0 [$^1J$($^{13}$C−$^1$H) = 146.5 Hz, *C*H$_2$]; 20.9 (CH*Me*); 12.8 (P*Me*$_3$). $^{31}$P NMR ($C_6D_6$, 30 °C): major isomer $\delta$ 2.19 (*P*Me$_3$); minor isomer $\delta$ 1.40 (*P*Me$_3$).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$CHMe)(PMe$_2$Ph)] (15b).** Anal. Calcd for $TiC_{47}H_{43}O_2P$: C, 78.54; H, 6.03; P, 4.31. Found: C, 75.23; H, 5.88; P, 3.02. $^1$H NMR ($C_6D_6$, 30 °C): major isomer $\delta$ 6.73−7.59 (aromatics); 1.46 (d, 6.2 Hz, CH*Me*); 1.63 (m), 1.47 (m, C$H_2$); 0.41 (m, C*H*Me); 0.64 (d), 0.26 (d, 5.8 Hz, P*Me*$_2$Ph); minor isomer $\delta$ 2.23 (m, C*H*Me); 1.13 (d, 6.4 Hz, CH*Me*); 1.00 (m), 0.4 (m, C$H_2$); 0.36 (d, 6.4 Hz, P*Me*$_2$Ph). $^{13}$C NMR ($C_6D_6$, 30 °C): major isomer $\delta$ 81.8 [d, $^1J$($^{13}$C−$^1$H) = 146.2 Hz, $^2J$($^{13}$C−$^{31}$P) = 2.6 Hz, Hz, *C*H$_2$]; 77.5 [$^1J$($^{13}$C−$^1$H) = 148.3 Hz, *C*HMe]; 22.6 (CH*Me*); minor isomer $\delta$ 90.0 (*C*H$_2$); 76.2 (*C*HMe). $^{31}$P NMR ($C_6D_6$, 30 °C): major isomer $\delta$ 14.8 (PMe$_2$-PH); minor isomer $\delta$ 11.4 (PMe$_2$Ph).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CHPhCH$_2$)(PMe$_2$Ph)] (17).** $^1$H NMR ($C_6D_6$, 30 °C): major isomer $\delta$ 6.50−7.40 (aromatics); 2.20 (ddd), 1.79 (ddd, 12 Hz, 7Hz, C$H_2$); 1.10 (t, 12 Hz, C*H*Ph); 0.63 (d), 0.03 (d, 7.2 Hz, P*Me*$_2$Ph); minor isomer $\delta$ 2.70 (dd, 12 Hz, C*H*Ph); 0.98 (dd), 0.22 (dd, 12 Hz, 6 Hz, C$H_2$); 0.46 (d), −0.02 (d, 7.3 Hz, P*Me*$_2$Ph). $^{13}$C NMR ($C_6D_6$, 30 °C): major isomer $\delta$ 159.5 (Ti−O−C); 159.3 (Ti−O−C); 93.1 [d, $^2J$($^{13}$C−$^{31}$P) = 2.9 Hz, *C*H$_2$]; 78.1 (*C*HPh); minor isomer $\delta$ 160.1 (Ti−O−*C*); 159.8 (Ti−O−*C*); 83.3 (*C*H$_2$); 80.1 [d, $^2J$($^{13}$C−$^{31}$P) = 5.3 Hz, *C*HPh]. $^{31}$P NMR ($C_6D_6$, 30 °C): major isomer $\delta$ 15.2 [$^3J$($^{31}$P−$^1$H) = 7.0 Hz, *P*Me$_2$Ph]; minor isomer $\delta$ 13.5 [$^3J$($^{31}$P−$^1$H) = 6.0 Hz, *P*Me$_2$Ph].

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(OCPh$_2$CH$_2$CH$_2$CH$_2$CH$_2$)] (18).** Anal. Calcd for $TiC_{59}H_{50}O_3$ **18**·$C_6H_6$: C, 82.90; H, 5.85. Found: C, 82.61; H, 6.14. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.88−7.42 (aromatics); 2.22 (m, C$H_2$CPh$_2$); 1.44 (m, TiCH$_2$C$H_2$); 1.21 (m, C$H_2$CH$_2$CPh$_2$); 1.04 (m, TiC$H_2$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 159.6 (Ti−O−C); 94.1 (O*C*Ph$_2$); 87.5 (Ti*C*H$_2$); 43.4 (TiCH$_2$*C*H$_2$); 32.4, 26.3 (*C*H$_2$CH$_2$CPh$_2$).

**Preparation of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(OCPh$_2$CH$_2$CH$_2$)] (19).** Anal. Calcd for $TiC_{51}H_{40}O_3$: C, 81.81; H, 5.38. Found C, 81.62; H, 5.20. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.85−7.38 (aromatics); 3.34 (t), 1.47 (t, 6.6 Hz C$H_2$). Selected $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 160.0 (ipso O*Ar*′′); 148.8 (ipso OC*Ph*$_2$); 92.4 (TiO*C*Ph$_2$); 82.2 [$^1J$($^{13}$C−$^1$H) = 132.2 Hz, Ti*C*H$_2$]; 53.0 [$^1J$($^{13}$C−$^1$H) = 131.0 Hz, TiCH$_2$*C*H$_2$].

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(OCPh$_2$CH$_2$CH$_2$CPh$_2$O)] (20).** Anal. Calcd for $TiC_{64}H_{50}O_4$: C, 82.57; H, 5.41. Found: C, 82.82; H, 5.52. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.78−7.41 (aromatics); 2.51 (s, C$H_2$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 160.0 (Ti−O−C); 95.1 (TiO*C*Ph$_2$); 38.0 (*C*H$_2$).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${OCPh$_2$CH$_2$CH(C$_4$H$_8$)CHCH$_2$}] (21).** Anal. Calcd for $TiC_{57}H_{50}O_3$: C, 82.39; H, 6.07. Found: C, 82.61; H, 6.16. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.83−7.71 (aromatics): 2.37 (dd, 16 Hz, 8 Hz), 2.18 (d, C$H_2$CPh$_2$); 0.63−1.38 (m, other aliphatic protons); 0.40 (bdd), 0.22 (bdd, Ti*CH*$_2$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 160.0, 159.0 (Ti−O−C); 97.5 (O*C*Ph$_2$); 93.1 (Ti*C*H$_2$); 52.5 (OCPh$_2$*C*H$_2$); 49.3, 39.6 (*C*H); 37.8, 37.6, 26.8, 26.6 (CH*C*H$_2$*C*H$_2$).

**Reaction of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${C$_4$H$_6$(Ph)$_2$}] (7) with Ph$_2$C═O.** A sample of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${C$_4$H$_6$(Ph)$_2$}] (**7**) was dissolved in benzene-$d_6$ (1 mL) in a J. Young valve solvent sealed NMR tube. To this solution was added solid benzophenone. The $^1$H NMR at 30 °C of the resulting dark red solution was immediately obtained and contains **22**, **23** and **24**: $\delta$ 6.50−7.80 (aromatics); 5.62 (broad d), 5.10 (broad d, PhC*H*═C*H*$_2$); 4.51 (broad, Ti−OCPh$_2$C*H*Ph of **24**); 3.71 (t, TiC*H*Ph of **23**); 3.20−3.45 (m, TiCHPhC*H*$_2$ of **23**); 3.38 (dd), 3.01 (broad d, Ti-OCPh$_2$C*H*$_2$ of **24**). Over the course of one day, or if more benzophenone was added, the solution became light orange in color. The $^1$H NMR of this solution showed that the signals for **23** had disappeared and the $^1$H NMR signals for **24** had become more intense.

**Reaction of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${C$_4$H$_6$(Ph)$_2$}](7) with Ph$_2$$^{13}$C═O.** A sample of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${C$_4$H$_6$(Ph)$_2$}] (**7**) was placed in a J. Young valve solvent sealed NMR tube along with benzene-$d_6$ (1 mL). To this was added one crystal of solid $^{13}$C-labeled benzophenone. The $^{13}$C NMR, at 30 °C, of the resulting red solution clearly shows the presence of **22*** ($\delta$ 112.8), **23*** ($\delta$ 90.3), and **24*** ($\delta$ 99.0 and 97.5). As more benzophenone was added (one crystal at a time) the signal at $\delta$ 90.3 disappeared and the signals at $\delta$ 112.8, 99.0, and 97.5 increased in intensity. This corresponds to the same trend seen in the $^1$H NMR above using natural abundance benzophenone.

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(OCPh$_2$)(PMe$_3$)] (25).** Anal. Calcd for TiC$_{52}$H$_{45}$O$_3$P: C, 78.38; H, 5.69; P, 3.89. Found: C, 79.27; H, 5.90; P, 3.73. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.79−7.49 (aromatics); −0.23 (d, PMe$_3$). $^{13}$C NMR (C$_6$D$_6$, 30 °C: $\delta$ 160.5 (Ti−O−C); 91.4 (*C*Ph$_2$); 12.0 (d, P*Me*$_3$). Hydrolysis product Ph$_2$CHOH: $^1$H NMR (C$_6$D$_6$, 30 °C: $\delta$ 6.95−7.30 (aromatics) 5.48 (d, O*H*); 1.69 (d, C*H*).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(OCPh$_2$CH$_2$CHMe)] (26).** The major isomer was [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(OCPh$_2$CH$_2$CHMe)] while the minor isomer was [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(OCPh$_2$CHMeCH$_2$)]. $^1$H NMR (C$_6$D$_6$, 30 °C): major isomer $\delta$ 6.7−7.5 (aromatics); 3.25 (dd, 13 Hz, 12 Hz), 2.94 (dd, 14 Hz, 6 Hz, C*H*$_2$); 1.88 (m, C*H*Me); 0.60 (d, 6 Hz, CH*Me*); minor isomer $\delta$ 3.69 (m, C*H*Me); 1.12 (dd), 0.99 (dd, C*H*$_2$); 0.93 (d, CH*Me*). $^{13}$C NMR (C$_6$D$_6$, 30 °C): major isomer $\delta$ 159.7 (Ti−O−*C*); 149.4, 148.6 (ipso OC*Ph*$_2$); 95.4 (TiCHMe); 89.8 (TiO*C*Ph$_2$); 59.0 (*C*H$_2$); 21.8 (CH*Me*).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${N(CH$_2$Ph)CHPhCH$_2$CH(C$_4$H$_8$)CHCH$_2$}] (27).** Anal. Calcd for TiC$_{58}$H$_{53}$NO$_2$: C, 82.54; H, 6.33; N, 1.66. Found: C, 82.58; H, 6.27; N, 1.66. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.69−7.51 (aromatics); 4.30 (d), 3.01 (d, 15 Hz, C*H*$_2$Ph); 3.67 (d, 12 Hz, C*H*Ph); 2.58 (m, CHPhC*H*$_2$); 0.31 (m), 0.02 (m, TiC*H*$_2$); 0.70−1.50 (other aliphatic protons). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 160.5, 160.2 (Ti−O−*C*); 87.6 (Ti*C*H$_2$); 63.3 (N*C*HPh); 58.1 (N*C*H$_2$Ph); 48.1 (*C*H); 43.4, 39.6, 27.5, 27.1 (CH*C*H$_2$*C*H$_2$). Hydrolysis product BzNHCHPhCH$_2$-CH(C$_4$H$_8$)CH$_3$ $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.85−7.49 (aromatics); 3.63 (dd, C*H*$_2$Ph); 3.49 (q, N*H*); 0.77 (d, CH$_3$); 0.6−2.1 (other aliphatic protons). Mass spectroscopy: parent M$^+$ at 307 amu.

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${N(Ph)CHPhCHPhN(Ph)}] (28).** $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 5.84−7.60 (aromatics); 5.73, 5.00 (m's, olefinic 1,7-octadiene); 5.41, 4.93 (*s,s,cis*- and *trans*-NPhC*H*Ph); 2.00−1.00 (aliphatic 1,7-octadiene). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$73.7, 70.8 (*cis*- and *trans*-NPh*C*HPh).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2$(NPhCHPhCH$_2$CHPh)] (29).** Anal. Calcd for TiC$_{57}$H$_{45}$NO$_2$: C, 83.08; H, 5.51; N, 1.70. Found: C, 82.74; H, 5.63; N, 1.82. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.50−7.50 (aromatics); 5.91 (d), 5.47 (d, 7.7 Hz, *ortho*-N*Ph*); 4.37 (d, 3.7 Hz, TiNPhC*H*Ph); 3.32 (ddd, 16.2 Hz, 14.5 Hz, 5.2 Hz), 3.04 (dd, 14.3 Hz, 3.5 Hz, TiCHPhC*H*$_2$); 2.42 (d, 15.8 Hz, Ti*C*HPh). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 160.7, 160.1 (Ti−O−C); 107.5 (Ti*C*HPh); 59.0 (TiNPh*C*HPh); 30.7 (TiCHPh*C*H$_2$).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${N(CH$_2$Ph)CHPhCH$_2$CH$_2$}] (30).** Anal. Calcd for TiC$_{58}$H$_{49}$NO$_2$ **30**·C$_6$H$_6$: C, 82.94; H, 5.88; N, 1.67. Found: C, 82.63; H, 5.95; N, 2.05. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.63−7.43 (aromatics); 3.89 (d), 3.24 (d, 15.1 Hz, C*H*$_2$Ph); 3.75 (t, 6.9 Hz, C*H*Ph); 2.21 (m, TiCH$_2$C*H*$_2$); 1.39 (m), 1.15 (m, TiC*H*$_2$). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\partial$ 160.4, 160.1 (Ti−O−*C*); 85.9 (Ti*C*H$_2$); 64.2 (*C*HPh); 57.1; *C*H$_2$-Ph); 33.7 (TiCH$_2$*C*H$_2$). Hydrolysis product [PhCH$_2$NHCHPhCH$_2$CH$_3$] $^1$H NMR (C$_6$D$_6$, 30 °C): $\partial$ 7.08−7.30 (aromatics); 3.66 (d), 3.44 (d, 13.6 Hz, C*H*$_2$Ph); 3.41 (t, C*H*Ph); 2.7 (broad, N*H*); 1.63 (dq, C*H*$_2$); 0.70 (t, 7.4 Hz, C*H*$_3$). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 64.6 (*C*HPh); 51.8 (*C*H$_2$Ph); 31.4 (*C*H$_2$); 10.9 (*C*H$_3$).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${N(CH$_2$Ph)CHPhCHPhN(CH$_2$Ph)}] (31).** Anal. Calcd for TiC$_{64}$H$_{52}$N$_2$O$_2$: C, 82.74; H, 5.64; N, 3.02. Found: C, 82.83; H, 5.67; N, 3.02. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.25−7.69 (aromatics); 4.68 (s, CHPh); 3.99 (d), 2.99 (d, 16 Hz, CH$_2$Ph). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 160.6 (ipso O*Ar*″); 76.3 (*C*HPh); 55.7 (*C*H$_2$Ph).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${N(CH$_2$Ph)CHPhCEtCEt}] (32).** Anal. Calcd for TiC$_{56}$H$_{49}$NO$_2$: C, 82.44; H, 6.05; N, 1.72. Found C, 82.84; H, 6.27; N, 1.87. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.76−7.61 (aromatics); 4.35 (s, C*H*Ph); 3.14 (d), 2.90 (d, 15.7 Hz, C*H*$_2$Ph); 1.40 (q, 7.6 Hz), 1.26 (m, C*H*$_2$CH$_3$); 0.55 (t), 0.40 (t, 7.5 Hz, CH$_2$C*H*$_3$). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 218.2 (Ti*C*Et); 160.7, 160.4 (Ti−O−*C*); 139.8 (TiCEt*C*Et); 61.7 (*C*HPh); 55.5 (*C*H$_2$Ph); 27.2, 23.8 (*C*H$_2$CH$_3$); 14.8, 13.1 (CH$_2$*C*H$_3$). Hydrolysis product CHEt═CEtCHPhNHBz $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 7.04−7.42 (aromatics); 5.62 (t, 7.3 Hz, C*H*Et); 4.14 (s, C*H*Ph); 3.63 (dd, 16.9 Hz, 3.5 Hz, C*H*$_2$Ph); 1.97 (m, C*H*$_2$CH$_3$); 1.32 (broad, N*H*); 0.94 (t), 0.80 (t, 7.5 Hz, CH$_2$C*H*$_3$). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 68.7 (*C*HPh); 52.2 (*C*H$_2$Ph); 21.6, 21.4 (*C*H$_2$CH$_3$); 14.9, 14.5 (*C*H$_2$*C*H$_3$). HRMS: calcld for 280.2065, found 280.2062.

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${N(CH$_2$Ph)CHPhCHCPh}] (33).** Anal. Calcd for TiC$_{58}$H$_{45}$NO$_2$: C, 83.34; H, 5.43; N, 1.68. Found: C, 83.00; H, 5.54; N, 1.71. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.43−7.61 (aromatics): 6.74 (d, 3.1 Hz, CPhC*H*); 4.50 (d, 3.1 Hz, C*H*Ph); 3.23 (d); 3.05 (d, 15.8 Hz, C*H*$_2$Ph). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 207.5 (Ti*C*Ph); 160.9, 160.6 (Ti−O−*C*); 138.4 (CPh*C*H); 58.9 (*C*HPh); 56.6 (*C*H$_2$Ph). Hydrolysis product *trans*-CHPhCHCHPhNHBz $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 7.0−7.45 (aromatics); 6.51 (d, 15.8 Hz, C═C*H*Ph); 6.25 (dd, 15.8 Hz, 7.0 Hz, C*H*═C); 4.26 (d, 7.0 Hz, NC*H*Ph); 3.65 (s, NC*H*$_2$Ph); 1.89 (broad, N*H*). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 65.1 (*C*HPh); 51.8 (*C*H$_2$Ph). HRMS: calcd for 299.1674, found 299.1668.

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${NPhCHPhCHC(SiMe$_3$)}] (34).** Anal. Calcd for TiC$_{54}$H$_{47}$NO$_2$Si: C, 79.29; H, 5.80; N, 1.71. Found: C, 78.90; H, 6.06; N, 1.63. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 7.57 (d, *ortho*-Ph$_2$-2,6); 7.39 (d, 4.0 Hz, TiNPhCHPhC*H*); 6.40−7.30 (aromatics); 5.45 (d, *ortho*-N*Ph*); 4.62 (d, 4.0 Hz, TiNPhC*H*Ph); −0.25 [s, Si(C*H*$_3$)$_3$]. $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 228.4 (TiNPhCHPhCHC*C*SiMe$_3$); 160.7, 160.5 (Ti−O−*C*); 137.4 (TiNPhCHPh*C*H); 54.5 (TiNPh*C*HPh); −1.0 [Si-(*C*H$_3$)$_3$]. Hydrolysis product *trans*-Me$_3$SiCH═CHCHPhNHPh $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.60−7.30 (aromatics); 6.41 (d, *ortho*-N*Ph*); 6.10 [dd, $^3J$($^1$H−$^1$H) = 18.5 Hz and 5.0 Hz, Me$_3$SiCHC*H*]; 5.88 [d, $^3J$($^1$H−$^1$H) = 18.5 Hz, Me$_3$SiC*H*); 4.78 (b, Me$_3$SiCHCHC*H*Ph); 3.73 (broad d, N*H*Ph); −0.02 [s, Si(C*H*$_3$)$_3$].

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${NCPhCHPhN(CH$_2$Ph)}] (35).** Anal. Calcd for TiC$_{63}$H$_{50}$N$_2$O$_2$ **35**·C$_6$H$_6$: C, 82.70; H, 5.51; N, 3.06. Found: C, 83.32; H, 5.78; N, 2.99. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 6.73−7.62 (aromatics); 5.81 (s, C*H*Ph); 3.72 (d), 2.96 (d, 15.8 Hz, C*H*$_2$Ph). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 186.4 (TiN*C*Ph); 161.4, 160.7 (ipso *OAr*″); 90.6 (*C*HPh); 53.5 (*C*H2Ph).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6){NHCPhCPhN(CH$_2$Ph)}] (36).** A sample of [Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${NCPhCHPhN(CH$_2$Ph)}] (**30**, 0.50 g, 0.62 mmol) was dissolved in benzene (10 mL). A small amount of PhCN was added, and the solution was refluxed for 1 h. Excess solvent was removed under vacuum, and the product **36** was recovered as a dark red oil. Selected $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 159.2 (Ti−O−*C*); 117.0, 115.0 (*C*Ph*C*Ph); 58.4 (*C*H$_2$Ph).

**[Ti(OC$_6$H$_3$Ph$_2$-2,6)$_2${NHCPhCPhN(CH$_2$Ph)}(py)] (37).** Anal. Calcd for TiC$_{62}$H$_{49}$N$_3$O$_2$: C, 81.30; H, 5.39; N, 4.59. Found: C, 81.67; H, 5.57; N, 4.49. $^1$H NMR (C$_6$D$_6$, 30 °C): $\delta$ 9.91 (broad, N*H*); 6.13−7.60 (aromatics); 4.62 (s, C*H*$_2$Ph). $^{13}$C NMR (C$_6$D$_6$, 30 °C): $\delta$ 160.6 (ipso O*Ar*″); 56.4 (*C*H$_2$Ph).

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**Supporting Information Available:** Experimental details of the synthesis of new compounds; 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 **4**, **7**, **10**, **12**, **14a**, **25** and **35** (172 pages). See any current masthead page for ordering information and Internet access instructions.

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