The Chemistry of Titanacyclopentadiene Rings Supported by 2,6-Diphenylphenoxide Ligation: Stoichiometric and Catalytic Reactivity

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The sodium amalgam (two Na per Ti) reduction of hydrocarbon solutions of $[Ti(OAr'')_2Cl_2]$ (OAr'' = 2,6-diphenylphenoxide) in the presence of EtC≡CEt, Bu^{t}C≡CH, and MeC≡CPh (≥2 equiv) produces the corresponding titanacyclopentadiene complexes $[(Ar''O)_2Ti(C_4Et_4)]$ (**1**), $[(Ar''O)_2(C_4H_2Bu^t_2)]$ (**2**), and $[(Ar''O)_2Ti(C_4Me_2Ph_2)]$ (**3**). The use of less bulky substituents on the alkyne substrate in such reactions leads to mixtures of aromatic compounds due to cyclotrimerization reactions. The solid state structure of **1** shows a pseudotetrahedral environment about the titanium metal center with a planar titanacyclopentadiene ring. The ^{1}H and ^{13}C NMR spectra of solutions of **1–3** show no exchange of α- and β-positions of the metallacycle rings. Only the 2,4-regioisomer of **2** and **3** was detected in solution. Reaction of **1** with PhC≡CPh produced $[(Ar''O)_2Ti(C_4Ph_4)]$ (**4**). Reaction of **1–4** with protic reagents yielded the corresponding diene derivatives while iodination of **1** and **2** yielded 1,4-diiodo-1,3-butadienes. Compounds **1–4** will catalyze the cyclotrimerization of a range of alkynes. Terminal alkynes with small substituents produce the 1,2,4-trisubstituted benzene preferentially in an exothermic reaction. The more bulky substrates Bu^{t}C≡CH and Me$_3$SiC≡CH react more slowly and only the symmetrical 1,3,5-isomer is produced. The reaction of the titanacyclopentadiene rings in **1** and **2** with a variety of unsaturated organic molecules has been investigated. Reaction of **1** with Bu^{t}NC leads to a new organometallic compound **5** containing an η^2-C,N-bound cyclopentadiene–imine which was structurally characterized as a pyridine adduct (**7**). The solid state structure of **7** showed a structure related to other titanium η^2-C,N-bound imine complexes, but with a long Ti—C distance of 2.262(3) Å. Reaction of **1** or **2** with benzonitrile leads to the elimination of 1 equiv of the corresponding pyridine. The organometallic product of these reactions was identified as a dimeric material $[(Ar''O)_2Ti(\mu\text{-}PhCN)_2Ti(OAr'')_2]$ (**8**) containing two bridging benzonitrile ligands. The solid state structure of **8** showed the bridging PhCN unit to be highly reduced and strongly bound to the titanium metal centers. The lack of reactivity of **8** precluded the catalytic formation of pyridines. Both compounds **1** and **2** undergo ring expansion with Ph_2CO at 25 °C to form the corresponding 2-oxatitanacyclohepta-4,6-diene derivatives **9** and **10**. In **10** the ketone was found to insert into the side of the titanacyclopentadiene ring containing the less bulky substituent, leading to a single regioisomer. Reaction of **1** with Ph_2CO at 100 °C led to the 2-oxatitanacyclopent-4-ene complex $[(Ar''O)_2Ti(OCPh_2CEtCEt)]$ (**11**) along with 1 equiv of 3-hexyne. Attempts to interconvert **9** and **11** failed. Further elaboration of the seven membered ring in **9** by reaction with Bu^{t}NC yielded the η^2-iminoacyl derivative **12**. The conformation of the large metallacycle rings in **9** and **12** was analyzed by carrying out single crystal X-ray diffraction analyses. Crystal data: at 20 °C for $TiO_2C_{48}H_{46}$ (**1**) a = 12.627(3) Å, b = 17.378(4) Å, c = 17.739(3) Å, α = 90.41(2)°, β = 94.68(2)°, γ = 92.89(2)°, Z = 4, d_{calcd} = 1.205 g cm^{-3} in space group $P\bar{1}$; for $TiO_2N_2C_{58}H_{60}$ (**7**) at −105 °C a = 12.554(4) Å, b = 17.934(5) Å, c = 21.567(6) Å, β = 102.38(2)°, Z = 4, d_{calcd} = 1.211 g cm^{-3} in space group $P2_1/n$; for $Ti_2O_4N_2C_{98}H_{74}$ (**8**) at −50 °C a = 23.100(4) Å, b = 12.656(3) Å, c = 27.486(7) Å, β = 109.09(2)°, Z = 4, d_{calcd} = 1.259 g cm^{-3} in space group $C2/c$; for $TiO_3C_{68}H_{64}$ (**9**) at −50 °C a = 12.147(3) Å, b = 12.527(3) Å, c = 20.363(3) Å, α = 80.92(2)°, β = 80.94(2)°, γ = 61.78(2)°, Z = 2, d_{calcd} = 1.204 g cm^{-3} in space group $P\bar{1}$; for $TiO_3NC_{66}H_{65}$ (**12**) at −20 °C a = 11.774(1) Å, b = 22.775(3) Å, c = 20.137(4) Å, β = 98.320(9)°, Z = 4, d_{calcd} = 1.203 g cm^{-3} in space group $P2_1/n$.

Introduction

The known organometallic chemistry of the group 4 metals Ti, Zr, and Hf has been dominated by the use of cyclopentadienyl and substituted cyclopentadienyl ligation.[1] In particular the last 15 years has seen the emergence of an extensive and rapidly expanding body of research dealing with the reaction chemistry associated with the metallocene, $[Cp_2M]$, unit.[2] Recent work in this area has focused on the use of group 4 metallocene derivatives as reagents for selective carbon–carbon bond forming reactions[3–7] and the involvement of cationic metallocene compounds in olefin oligomerization and polymerization reactions.[8–10] During the last 10 years our group has been exploring the use of bulky aryloxide ligation to support organometallic chemistry at early d-block metal centers.[11]

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In the case of the group 4 metals, both complementary and novel stoichiometric reactivity has been developed at bis(aryloxide) metal centers.[12]

The fragment $[(ArO)_2M]$ can be formally considered isoelectronic with $[Cp_2M]$ if the aryloxide oxygen atom donates a full six electrons to the metal center. However, for the group 4 metals, the flexible electron donating potential of the aryloxide ligands allows ready expansion of the coordination sphere, e.g. to six as in $[(ArO)_2ZrMe_2(bpy)]$[13a] and $[(ArO)_2Zr(\eta^2\text{-}Bu^tNCCH_2Ph)_2]$.[13b] Expansion of the coordination sphere in metallocene analogues is more difficult, hence possibly cutting out certain reaction pathways available for electronically more flexible aryloxide and related derivatives. This paper reports some of the chemistry associated with a series of titanacyclopentadiene compounds containing ancillary aryloxide ligation. These metallacyclic compounds exhibit an extensive stoichiometric reactivity as well as catalytic reactivity that has not been demonstrated for their direct metallocene counterparts.

Results and Discussion

Synthesis and Characterization of Titanacyclopentadiene Compounds. The titanacyclopentadiene compounds **1–3** were all obtained by the room temperature sodium amalgam reduction (two Na per Ti) of hydrocarbon solutions of the dichloride compound $[(Ar''O)_2TiCl_2]$ (Ar''O = 2,6-diphenylphenoxide)[14] in the presence of the particular alkyne substrate (Scheme I). The initially bright red mixtures become deep-purple over a 30-min period due to the formation of the dinuclear intermediate $[(Ar''O)_2Ti(\mu\text{-}Cl)_2Ti(OAr'')_2]$.[15] The purple color slowly fades over 12 h with the formation of dark-brown suspensions containing the crude metallacyclic products which can be isolated by simple filtration and recrystallization from hexane solution. Attempts to obtain analogous titanacyclopentadiene compounds using less bulky alkyne substrates such as 2-butyne or phenylacetylene were unsuccessful due to the rapid cyclotrimerization of the alkyne substrate under the reaction conditions (*vide infra*).

The reductive-coupling method also failed to produce the corresponding metallacyclic compound when diphenylacetylene was used as substrate. The reason for this is unclear as the compound $[(Ar''O)_2Ti(C_4Ph_4)]$ (**4**) was obtained by reacting compound **1** with PhC≡CPh in solution at 100 °C (Scheme I). It is interesting to note that when this reaction is carried out in a sealed, 5-mm NMR tube in C_6D_6, 3-hexyne (EtC≡CEt) is detected as one of the products.

A single crystal X-ray diffraction analysis of the tetraethyl-substituted derivative **1**[12e] confirmed the general structure of these titanacyclopentadiene compounds (Figure 1, Table I) and is discussed in detail later. The ^1H and ^{13}C NMR spectra of **1–4** in C_6D_6 solution show many similar features. The aromatic region of the spectra for **1–4** and all other organometallic compounds in this study is dominated by signals due to the 2,6-diphenylphenoxide ligands. A complex overlapping set of multiplets is typically seen for these ligands at δ 6.3–8.4 ppm in the ^1H NMR spectrum. In the ^{13}C NMR spectrum, the only readily assigned, and sometimes structurally informative, aryloxide signals are due to the Ti–O–*C ipso* carbons of the central phenoxy rings. These *ipso* carbons resonate

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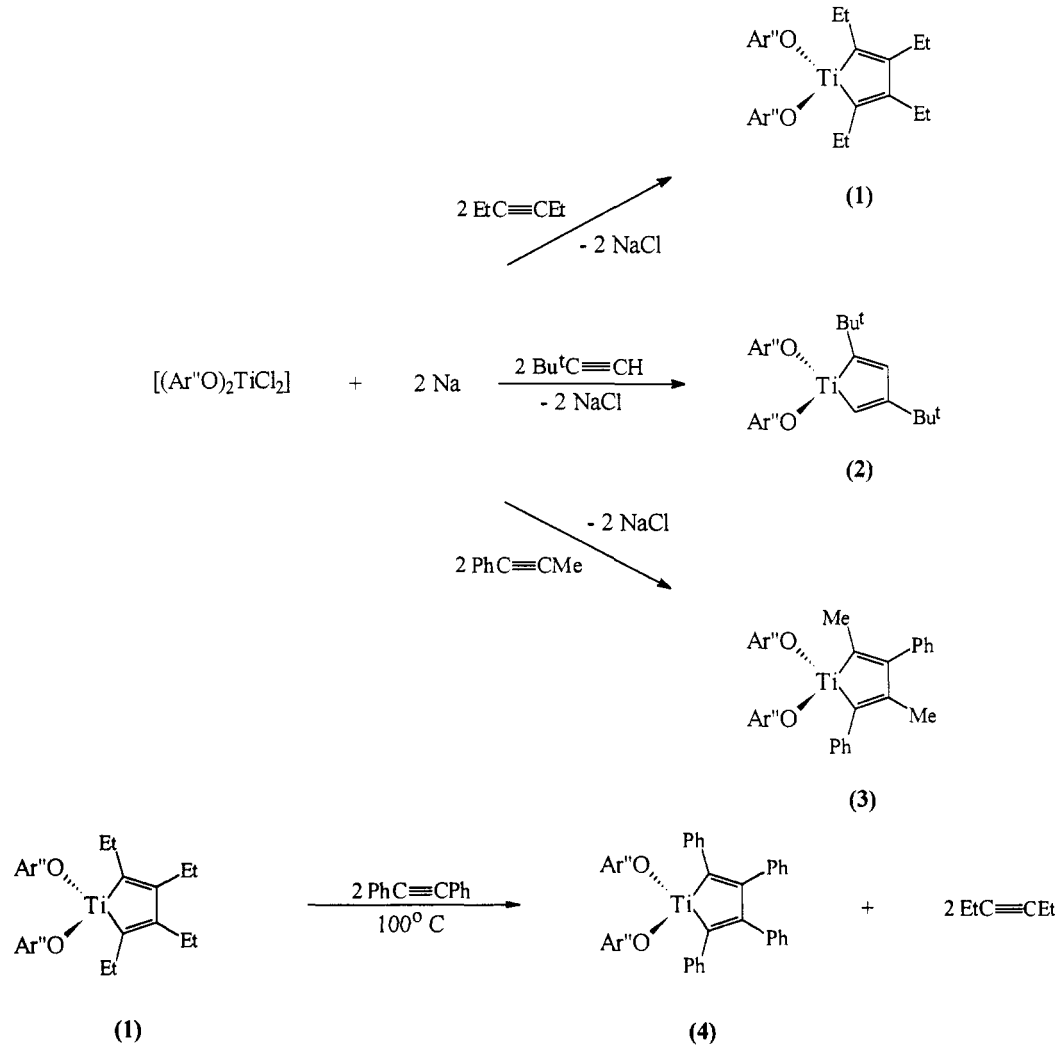
Scheme I



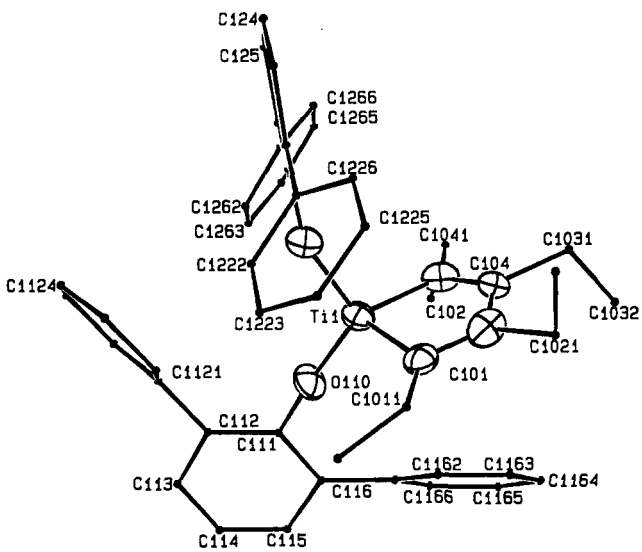


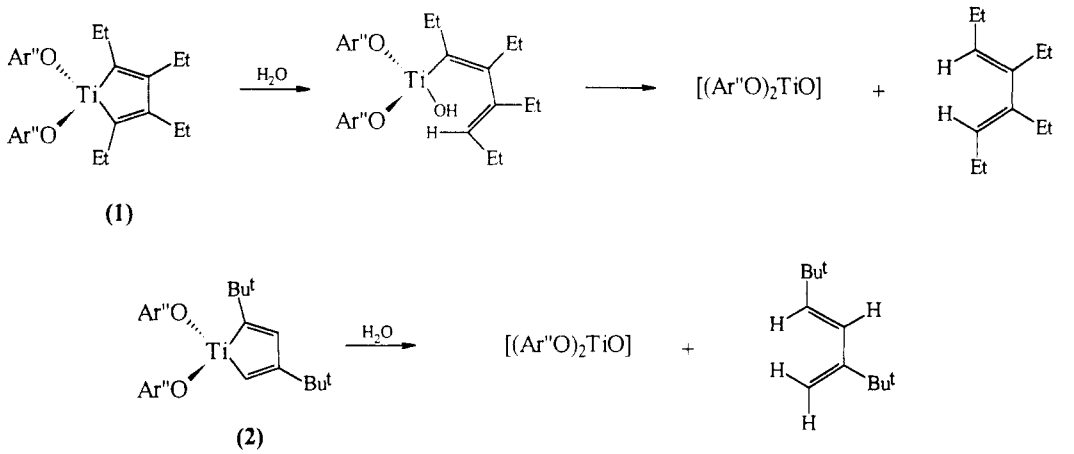
Figure 1. ORTEP view of $[(Ar''O)_2Ti(C_4Et_4)]$ (1) with hydrogen atoms omitted and emphasizing the central coordination sphere.

Table I. Selected Bond Distances (Å) and Angles (deg) for $[(Ar''O)_2Ti(C_4Et_4)]$ (1)

Molecule 1			
Ti(1)–O(110)	1.806(6)	Ti(1)–O(120)	1.804(6)
Ti(1)–C(101)	2.016(9)	Ti(1)–C(104)	1.986(9)
C(101)–C(102)	1.35(1)	C(102)–C(103)	1.52(1)
C(103)–C(104)	1.33(1)		
O(110)–Ti(1)–O(120)	116.5(3)	C(101)–Ti(1)–C(104)	94.3(4)
Ti(1)–C(101)–C(102)	99.9(7)	Ti(1)–C(104)–C(103)	100.4(7)
C(101)–C(102)–C(103)	121.1(9)	C(102)–C(103)–C(104)	122.7(9)
Ti(1)–O(110)–C(111)	175.7(6)	Ti(1)–O(120)–C(121)	155.8(6)
Molecule 2			
Ti(2)–O(210)	1.788(6)	Ti(2)–O(220)	1.828(6)
Ti(2)–C(201)	1.983(9)	Ti(2)–C(204)	2.02(1)
C(201)–C(202)	1.33(1)	C(202)–C(203)	1.55(1)
C(203)–C(204)	1.34(1)		
O(210)–Ti(2)–O(220)	111.1(3)	C(201)–Ti(2)–C(204)	98.5(4)
Ti(2)–C(201)–C(202)	95.8(7)	Ti(2)–C(204)–C(203)	92.7(7)
C(201)–C(202)–C(203)	123.0(9)	C(202)–C(203)–C(204)	122.6(9)
Ti(2)–O(210)–C(211)	165.9(6)	Ti(2)–O(220)–C(221)	165.9(6)

very close to δ 160 ppm, and can indicate whether the 2,6-diphenylphenoxide ligands are equivalent or not. In the ^1H and ^{13}C NMR spectra of 1, two (α and β) nonequivalent CH_2Me groups are present. No evidence for exchange of the nonequivalent α- and β-ethyl substituents of the metallacycle ring is observed in the ^1H NMR spectra of 1 at temperatures up to 80 °C. Hence, although the reactivity (*vide infra*) of 1 indicates that fragmentation of the metallacycle ring back into its two alkyne units can occur, this process has too high a barrier to be detected on the ^1H NMR time scale. There exist a large number of examples of group 4 metallacyclopentadiene compounds containing the metallocene unit $[Cp_2M]$

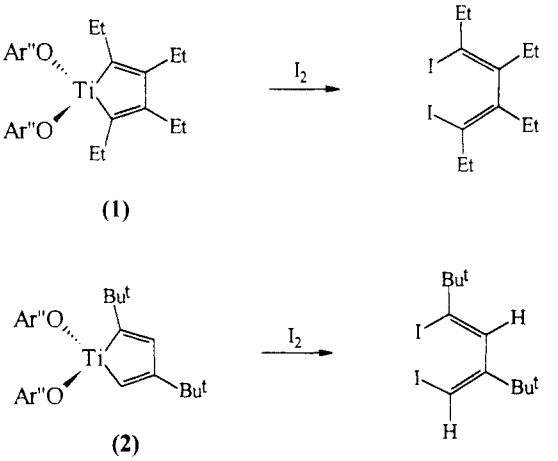
Scheme II



(M = Ti, Zr, Hf).[16-18] The α- and β-carbon atoms of the metallacycle rings in these compounds exhibit very characteristic chemical shifts in the ^{13}C NMR spectra and little variation is observed even as the central metal atom changes. For example, in the series $[Cp_2MC_4Ph_4]$, the α (and β) carbon atoms resonate at δ 202.1 (147.2), 193.8 (147.7), and 196.5 (148.5) ppm, respectively, for M = Ti, Zr, and Hf. In the case of the aryloxide compounds obtained in this study, the α-carbon atoms resonate downfield of the position found for their metallocene analogues, δ 225.0 ppm for $[(Ar''O)_2Ti(C_4Ph_4)]$ (**4**), possibly reflecting the more electron deficient nature of the metal center. Two nonequivalent Ti–C(α) resonances are observed for compounds **2** and **3** consistent with their formulation as 2,4-regioisomers. In the case of $[(Ar''O)_2Ti(C_4Bu^t_2H_2)]$ (**2**), two peaks at δ 240.6 and 202.3 ppm are observed in the ^{13}C NMR spectra. The higher field resonance appears as a doublet of doublets under proton coupling with $^1J(^{13}C-^1H)$ = 158.0 Hz and $^3J(^{13}C-^1H)$ = 63 Hz. The two protons bound directly to the ring in **2** appear as two doublets at δ 7.25 and 7.72 ppm in the ^1H NMR spectra with $^4J(^1H-^1H)$ = 4.4 Hz. The spectroscopic data for **1–4** are strong evidence that these compounds contain stable titanacyclopentadiene rings in solution and certainly are inconsistent with their formulation as bis(alkyne) complexes.

The reaction of the titanacyclopentadiene compounds **1–4** with protic reagents yields the corresponding substituted 1,3-butadienes and various titanium products (Scheme II). The structure (^1H NMR) of the organic products obtained by hydrolysis of $[(Ar''O)_2Ti(C_4Bu^t_2H_2)]$ (**2**) and $[(Ar''O)_2Ti(C_4Me_2Ph_2)]$ (**3**) confirmed the assigned regiochemistry (Scheme II). Intermediate organometallic compounds were detected by ^1H NMR spectroscopy when the metallacyclic compounds were hydrolyzed in C_6D_6 solution. In the case of **1** the spectroscopic data were consistent with the formation of an intermediate titanium–hydroxy compound of formula $[(Ar''O)_2Ti(CEt{=}CEt{-}CEt{=}CEtH)(OH)]$ (Scheme II). In the case of complex **3** the intermediate exhibited ^1H NMR signals consistent with its formulation as $[(Ar''O)_2Ti(CMe{=}CPh{-}CMe{=}CPhH)(OH)]$ (terminal olefin proton not coupled to a C*Me* group), indicating preferential hydrolysis of the Ti—CPh bond over the Ti—CMe bond within **3**. The reaction of **1** with aniline has been shown to be a useful synthetic method for the formation of the corresponding bis(phenylamido) complex $[(Ar''O)_2Ti(NHPh)_2]$, which can be converted into a variety of terminal phenylimido derivatives of titanium.[19]

Scheme III



The iodination of the titanacyclopentadiene complexes **1** and **2** was also readily achieved to yield the corresponding 1,4-diiodo-1,3-butadiene derivatives (Scheme III). This contrasts with the reported reactivity of related tantalacyclopentadiene compounds containing aryloxide ligation where only one side of the metallacycle ring was found to react with I_2.[20]

Catalytic Cyclotrimerization of Alkynes by Titanacyclopentadiene Compounds. Reactivity Studies. The cyclotrimerization of alkynes into aromatic products

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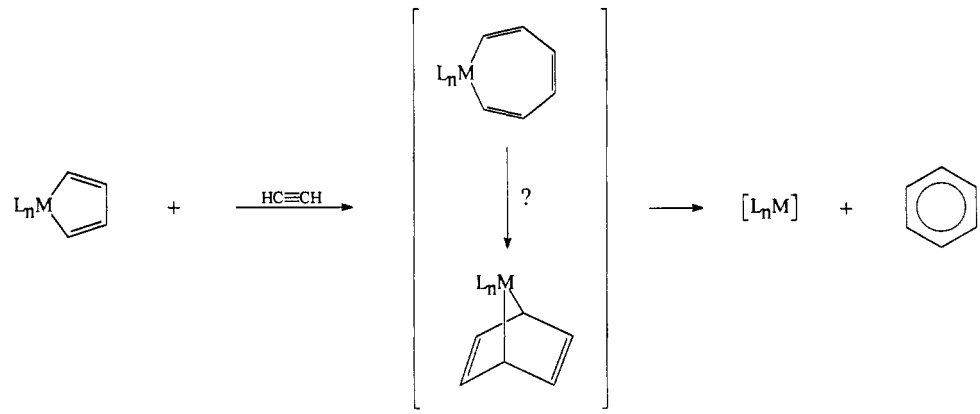
Scheme IV



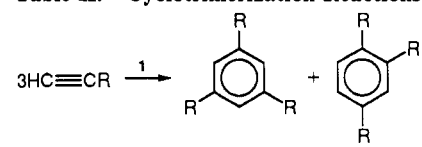
is one of the most ubiquitous catalytic reactions in organometallic chemistry.[21] Despite the large number of metallacyclopentadiene compounds containing the metallocene unit, $[Cp_2M]$ (M = Ti, Zr, Hf),[16-18] there are no reports of the involvement of such compounds in the catalytic oligomerization of alkynes. It appears that, once formed, further reaction of the metallacycle with alkynes does not readily occur. In contrast, the aryloxide containing titanacyclopentadiene complexes **1**–**4** will react with all but the most sterically protected alkynes to catalytically produce arene products (Scheme IV). We have investigated this reactivity in detail, focusing upon the use of the tetraethyltitanacyclopentadiene compound **1** as the catalyst precursor.

Solutions of compound **1** will react over days at 25 °C with 3-hexyne to catalytically produce hexaethylbenzene. The reaction occurs more rapidly at elevated temperatures and can be readily monitored by ^{1}H NMR spectroscopy in C_6D_6 solution. In a typical experiment a mixture of **1** with EtC≡CEt (25 equiv) in C_6D_6 was heated at 75 °C. Initially, signals due to the ethyl groups of only **1** and EtC≡CEt were present. Over time the intensity of the EtC≡CEt resonances decreased and were replaced by signals due to C_6Et_6 of equal intensity. No decrease occurred in the intensity of the signals of titanacyclopentadiene complex **1** during the course of the catalysis.

The reaction of **1** with other alkynes to produce cyclotrimerization producs is highly dependent upon the steric properties of the alkyne substituents. As mentioned previously, reactions of **1** with PhC≡CPh occur both slowly and stoichiometrically to produce $[(Ar''O)_2Ti(C_4Ph_4)]$ (**4**) along with 3-hexyne. Further reaction of **4** with excess PhC≡CPh does not occur to produce hexaphenylbenzene over days at 100 °C.

The reaction of **1** with phenylpropyne, PhC≡CMe, occurs slowly at room temperature to initially produce $[(Ar''O)_2Ti(C_4Me_2Ph_2)]$ (**3**) (^{1}H NMR) and 1 equiv of the substituted benzene C_6Et_4MePh (GC/MS). The catalytic cyclotrimerization of PhC≡CMe by **3** then occurs at a rate comparable to that found between EtC≡CEt and **1**. The cyclotrimerization of 20 equiv of phenylpropyne occurred over days at 25 °C to produce a 94:6 ratio of the 1,2,4- and 1,3,5-substitutional isomers of $C_6Me_3Ph_3$. No reaction between **1** and the alkyne substrate, PhC≡CEt, was observed after 1 day at 75 °C.

Table II.[a] Cyclotrimerization Reactions



R	mmol of HC≡CR	mmol of **2**	isomer ratios, % 1,3,5	1,2,4
$-C_6H_5$[b]	9.1	0.036	7	93
$-Pr^n$	1.5	0.043	28	72
$-Bu^n$	0.9	0.043	31	69
$-(c)C_5H_9$	1.8	0.071	30	70
$-Pr^i$	4.5	0.043	38	62
$-SiMe_3$	0.9	0.043	>95	<5
$-Bu^t$[c]	0.9	0.043	>95	<5

[a] Solvent is C_6D_6; products analyzed by ^{1}H NMR. All reactions were performed at room temperature unless noted. [b] The reaction was exothermic, proceeding to completion within minutes after addition of styrene to a solution of **2** in C_6D_6. [c] After 3 days of reaction time at room temperature, the sample was heated at 75 °C for 22 h.

These titanacyclopentadiene compounds prove to be highly efficient catalysts for the cyclotrimerization of terminal alkynes. The rate of the reaction as well as the ratio of unsymmetrical (1,2,4) to symmetrical (1,3,5) trisubstituted benzene was found to be dependent upon the steric size of the substituents attached to the alkyne. The reactivity of various terminal alkynes toward **1** was investigated by adding the alkyne (typically >20 equiv) to a solution of $[(Ar''O)_2Ti(C_4Et_4)]$ (**1**) in C_6D_6 and monitoring the reaction by ^{1}H NMR spectroscopy (Table II). The reaction of phenylacetylene with **1** was found to be exothermic, leading to the rapid formation of a 93:7 ratio of 1,2,4- and 1,3,5-$C_6H_3Ph_3$. In one experiment a total of 9.1 mmol (0.93 g, 250 equiv) of PhC≡CH was cyclotrimerized by 0.036 mmol (25 mg) of **1** in benzene after minutes. Workup of the product by chromatography on silica yielded a mixture of triphenylbenzenes (0.92 g). The dominant (93%) 1,2,4-substitutional isomer is readily separated from the minor component by recrystallization.

The aliphatic terminal alkynes RC≡CH (R = Pr^n, Bu^n, Pr^i, c-C_5H_9, $SiMe_3$, Bu^t) undergo cyclotrimerization by **1** as shown (Table II). The reactions of Bu^tC≡CH or Me_3SiC≡CH are slow at 25 °C occurring over days and hours, respectively, to produce exclusively the symmetrically

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1,3,5-trisubstituted benzene product. During the reaction of **1** with $Bu^tC{\equiv}CH$, the compound **2** was formed in the reaction mixture and detected by ^1H NMR spectroscopy. The other terminal alkynes undergo rapid cyclotrimerization by solutions of **1** at 25 °C to produce mixtures of the two substituted benzenes (Table II). After 20 equiv of 1-pentyne had been completely cyclotrimerized, the majority of the tetraethyltitanacycle **1** was still present (^1H NMR) in solution. This indicates that reaction of $Pr^nC{\equiv}CH$ with the unisolated intermediate $[(Ar''O)_2Ti(C_4H_2Pr^n)_2]$ is much more rapid than with the catalyst precursor **1**.

Mechanistic Considerations. There has been extensive debate in the literature concerning the pathway of alkyne cyclotrimerization by transition metal compounds.[21,22] It is doubtful that a reaction that can be achieved using such diverse metal reagents will exhibit a universal mechanism. The most widely discussed aspect of the mechanism involves the intermediates involved in reacting a metallacyclopentadiene with 1 equiv of alkyne to generate the uncomplexed arene product. The key mechanistic question centers on whether the two new carbon–carbon bonds are formed in a stepwise (via a metallacycloheptatriene intermediate) or in a concerted fashion, analogous to a Diels–Alder reaction (Scheme IV). The possible intermediacy of cyclobutadiene complexes has also been a mechanistic concern. Recent work by Bianchini and Caulton et al. favors a concerted pathway for acetylene cyclotrimerization at iridium metal centers, with an η^4-benzene species characterized as the organometallic product of reacting $HC{\equiv}CH$ with an iridacyclopentadiene complex.[23] In the case of the high valent, early d-block metal tantalum, Wigley et al. have isolated both tantalacyclopentadiene and η^6-arene (tantalanorbornadiene) complexes supported by aryloxide ligation.[24] Again, these results were interpreted in terms of a concerted pathway for the reaction.

The oligomerization of alkynes at group 4 and group 5 metal centers has excellent precedence.[25–27] In a recent series of studies, Calderazzo and co-workers have investigated the reactivity of group 4 metal arene complexes containing tetrahaloaluminate ligands.[28,29] The results of this study did not, however, manage to differentiate whether the isolated η^4-cyclobutadiene compounds were true catalytic intermediates or were in equilibrium with a catalytically active titanacyclopentadiene species.[28,29]

The stoichiometric and catalytic reaction chemistry supported by the titanium aryloxide fragment $[(Ar''O)_2Ti]$ is rapidly being developed by our group.[12,30] A wide range of organometallic reaction types have already been demonstrated at the metal center. Specifically, it has been shown that ring expansion of titanacyclopentadiene (*vide infra*), titanacyclopent-3-ene, and titanacyclopentane rings to generate stable seven membered metallacycles occurs with unsaturated organic molecules. Intramolecular carbon–carbon bond formation (reductive-elimination) to produce organic fragments which remain bound to the metal center has also been demonstrated. Each step in the stepwise pathway for cyclotrimerization, therefore, has precedence. There is, however, strong evidence that these titanacyclopentadiene compounds react with olefins in a concerted manner (Scheme V).[30] The cyclohexa-1,3-diene products obtained by the selective (2 + 2 + 2) cycloaddition of 2 equiv of alkyne and olefin are best accounted for by concerted formation and subsequent isomerization of titananorbornene (titanium cyclohexa-1,3-diene) intermediates.[30] No products are observed resulting from β-hydrogen migration in an open metallacyclohepta-2,4-diene intermediate. In contrast the product of selective catalytic cross-coupling of 2,3-dimethyl-1,3-butadiene and α-olefins is generated by β-hydrogen elimination in an isolable, open metallacycle. No cyclohexene products of reductive elimination are observed (Scheme V). This contrast in reactivity strongly supports the idea of a concerted pathway for these cyclotrimerization reactions (Scheme VI). A reaction proceeding via a statistical (1:1:2) distribution of the three possible intermediate titanacyclopentadiene complexes with identical rates would yield a 3:1 ratio of 1,2,4- and 1,3,5-substitutional isomers.

In the case of the substrate $Bu^tC{\equiv}CH$, the 2,4-substituted titanacyclopentadiene **2** was isolated and shown to catalyze the formation of only 1,3,5-tri-*tert*-butylbenzene. Hence, in this case catalysis must proceed via a highly regioselective concerted addition of $Bu^tC{\equiv}CH$ to **2**. In this system the driving force for the high regioselectivity is presumably steric factors.

The usymmetrical alkyne $PhC{\equiv}CMe$ has also been shown to form a nonsymmetrical titanacyclopentadiene (**3**). However, cyclotrimerization of this alkyne leads to a 94:6 mixture of 1,2,4- and 1,3,5-substituted benzenes. The formation of the minor, symmetrical benzene product must proceed via **3**. The formation of the 1,2,4-substituted benzene could also be argued to proceed via **3** with the observed isomer ratio reflecting the regioselectivity of addition to the titanacyclopentadiene ring of **3** by $PhC{\equiv}CMe$. However, it is difficult to rationalize the observed isomer ratio on the basis of steric effects if the catalytic reaction proceeds only via **3**. An alternative is to invoke the presence of minor amounts of the symmetrical titanacyclopentadiene intermediates which react more rapidly with the third equivalent of alkyne than does **3**.

A similar situation is present for the rapid cyclotrimerization by **1** of terminal alkynes containing small alkyl substituents. Steric (and statistical) factors favor the 2,4-

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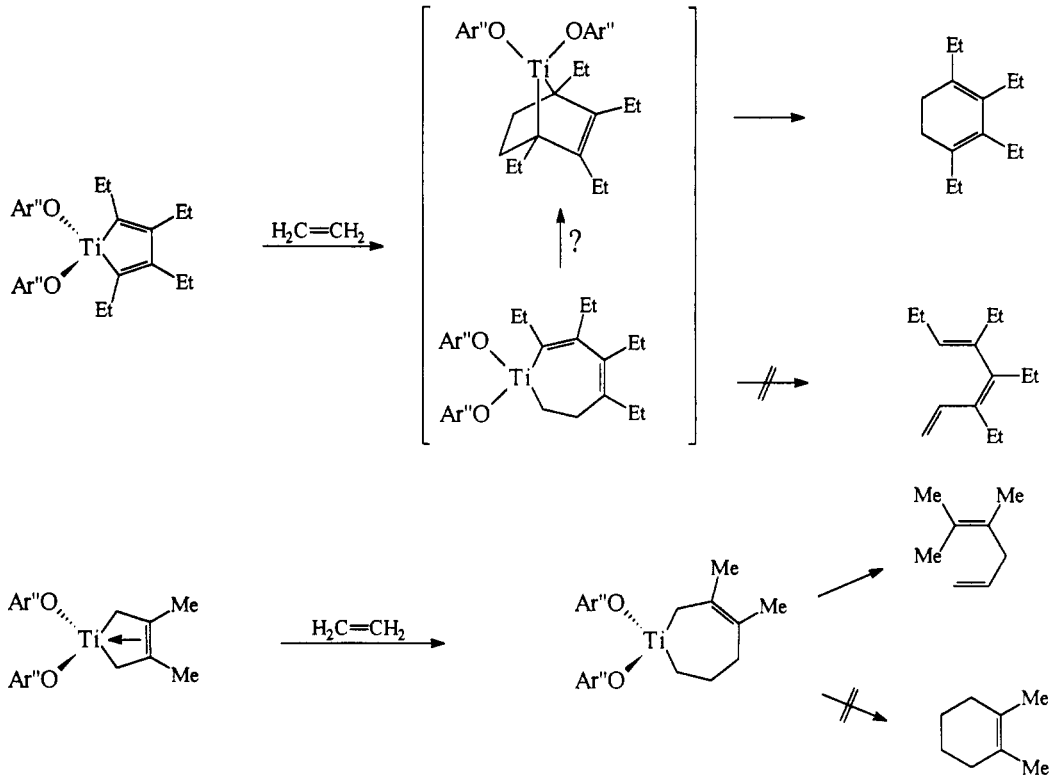
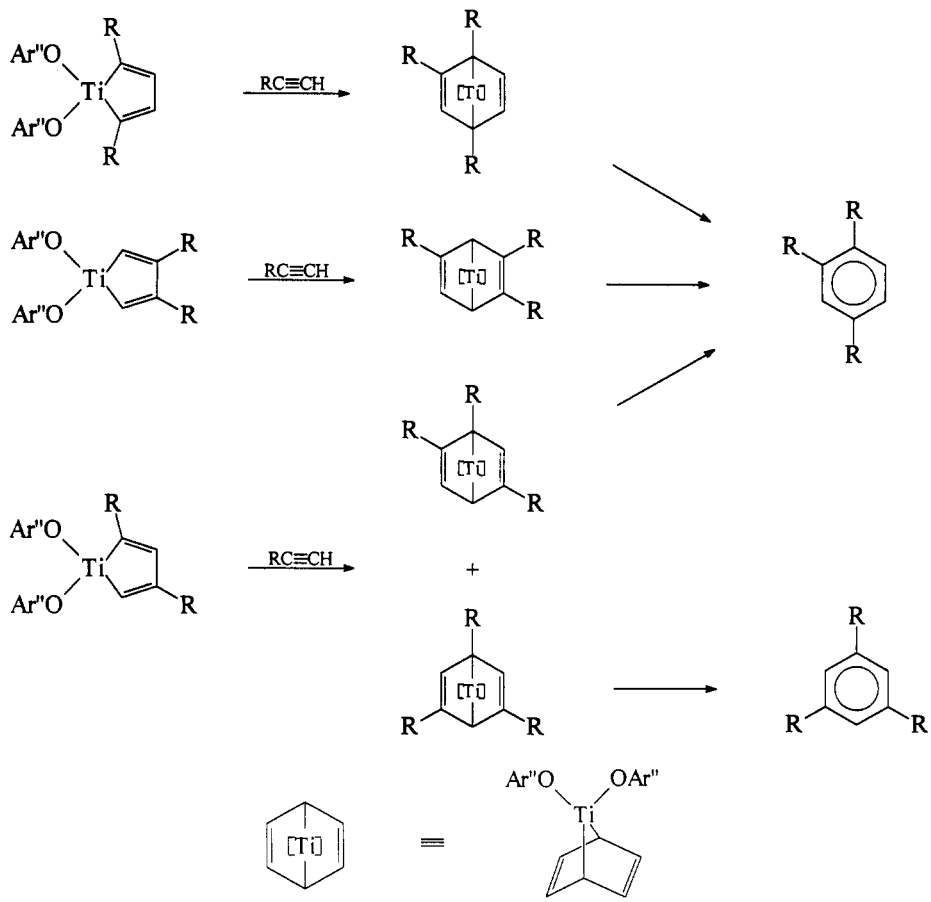
Scheme V



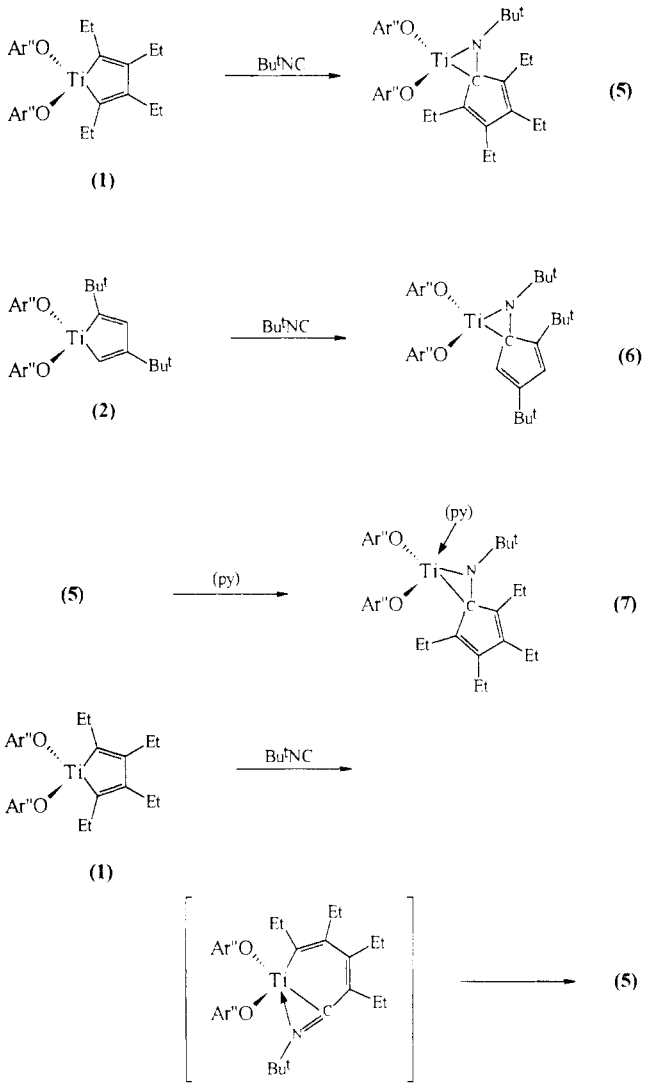
Scheme VI



disubstituted titanacyclopentadiene intermediate. The observed final product isomer ratio implies that if catalysis proceeds mainly through this intermediate, then the concerted pathway has to be highly regioselective, tolerating *cis* alkyl substituents during the addition.

Reaction with Organic Isocyanides. The titanacyclopentadiene complexes $[(Ar''O)_2Ti(C_4Et_4)]$ (1) and $[(Ar''O)_2Ti(C_4Bu^t_2H_2)]$ (2) react rapidly with Bu^tNC in benzene solution to produce the new organometallic products 5 and 6 (Scheme VII). The spectroscopic data

Scheme VII



for **5** and **6** are consistent with their formulation as η^2-imine complexes (Scheme VII). Compounds **5** and **6** proved difficult to handle, undergoing further reactions in solution. Addition of pyridine (py) to **5** yielded the adduct $[(Ar''O)_2Ti(\eta^2\text{-}Bu^tNCC_4Et_4)(py)]$ (**7**) which proved more amenable to study (Scheme VII). A single crystal X-ray diffraction study of **7** confirmed the presence of the metal-bound *tert*-butylimine of tetraethylcyclopentadieneone (Figure 2, Table III). The ^{13}C NMR data for **5–7** are informative. In these complexes a peak at δ 108.2, 116.5, and 115.2 ppm, respectively, can be assigned to the carbon atom of the η^2-bound imine. There is no evidence in the ^{13}C NMR spectra of **5** or **6** for their formulation as "open" metallacyclic intermediates (Scheme VII). This is significant, as previous work has shown that addition of 1 equiv of alkyl isocyanide (R'NC) to bis(alkyl) substrates $[(ArO)_2TiR_2]$ initially yields $[(ArO)_2Ti(\eta^2\text{-}R'NCR)(R)]$ which undergo ligand induced alkyl migration upon addition of pyridine to produce the η^2-imine compounds $[(ArO)_2Ti(\eta^2\text{-}R'NCR_2)(py)]$.[31] Presumably, the reaction of **1** and **2** with Bu^tNC proceeds in a stepwise manner via an open metallacyclic, η^2-iminoacyl intermediate (Scheme VII). This intermediate must rapidly undergo intramolecular reductive-elimination to produce **5** and **6**. An open metallacyclic η^2-iminoacyl (**12**) has been isolated and structurally characterized (*vide infra*), and the iminoacyl carbon is found to resonate at δ 240.8 ppm, a region characteristic of other titanium η^2-iminoacyl compounds. The hydrolysis of **5** or **7** yields the same organic product, which appears to be a tautomeric mixture of imines and enamines.

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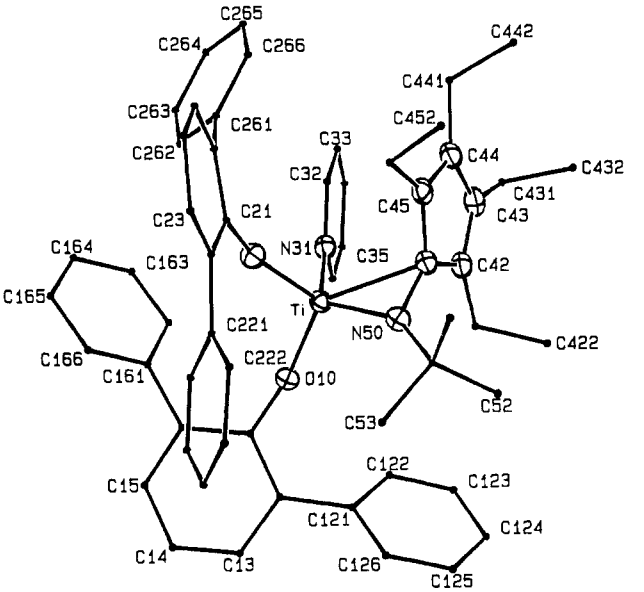


Figure 2. ORTEP view of $[(Ar''O)_2Ti(\eta^2\text{-}Bu^tNCC_4Et_4)(py)]$ (**7**).

Table III. Selected Bond Distances (Å) and Angles (deg) for $[(Ar''O)_2Ti(\eta^2\text{-}Bu^tNCC_4Et_4)(py)]$ (7)

Ti–O(10)	1.861(2)	Ti–O(20)	1.841(2)
Ti–N(50)	1.860(2)	Ti–C(41)	2.262(3)
Ti–N(31)	2.142(2)	C(41)–N(50)	1.417(3)
C(41)–C(45)	1.452(4)	C(42)–C(43)	1.378(4)
C(43)–C(44)	1.445(4)	C(44)–C(45)	1.385(4)
O(10)–Ti–O(20)	111.36(8)	O(10)–Ti–N(31)	95.20(8)
O(10)–Ti–N(50)	111.78(9)	O(10)–Ti–C(41)	132.67(9)
O(29)–Ti–N(31)	102.20(8)	O(20)–Ti–N(50)	113.21(9)
O(20)–Ti–C(41)	114.84(9)	N(31)–Ti–N(50)	121.51(9)
N(31)–Ti–C(41)	84.85(8)	N(50)–Ti–C(41)	84.85(8)
Ti–N(50)–C(41)	86.2(1)	Ti–C(41)–N(50)	55.1(1)
Ti–O(10)–C(11)	156.8(2)	Ti–O(20)–C(21)	153.5(2)

Reaction with Organic Nitriles. Reaction of **1** with acetonitrile takes place rapidly in benzene solution to yield 1 equiv of 2-methyl-3,4,5,6-tetraethylpyridine (^1H NMR and high resolution mass spectrometry) along with an unidentified titanium product. The treatment of **1** or **2** with benzonitrile similarly yielded 2-phenyl-3,4,5,6-tetraethylpyridine and 2-phenyl-4,6-di-*tert*-butylpyridine as the organic products (Scheme VIII). However, in these cases the titanium containing product was isolated and identified as a dinuclear compound $[(Ar''O)_2Ti(\mu\text{-}PhCN)_2Ti(OAr'')]_2$ (**8**) containing two bridging PhCN units. Dark red crystals of **8** were isolated from the reaction mixtures and subjected to a single crystal X-ray diffraction analysis (Figure 3, Table IV). The cotrimerization of alkynes and nitriles to produce the pyridine nucleus has been demonstrated many times both stoichiometrically and catalytically.[21a] Recent work by Wigley et al. on the reaction of a tantalacyclopentadiene with organic nitriles shows the resulting pyridine ring can sometimes remain strongly

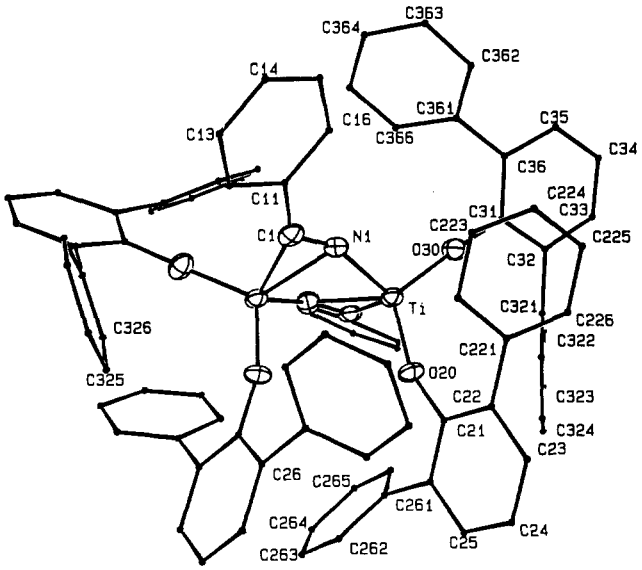
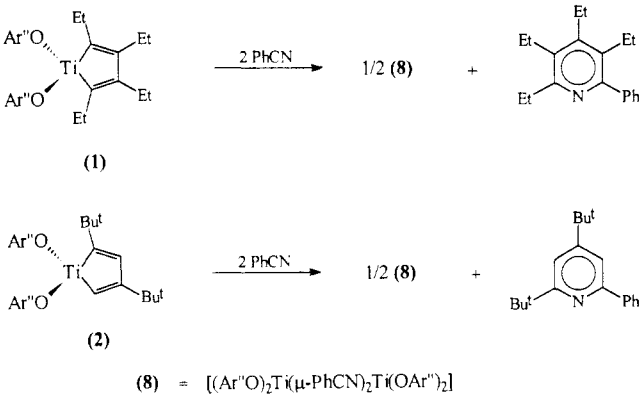


Figure 3. ORTEP view of $[(Ar''O)_2Ti(\mu\text{-}PhCN)_2Ti(OAr'')_2]$ (8).

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[(Ar''O)_2Ti(\mu\text{-}PhCN)_2Ti(OAr'')_2]$ (8)

Ti–Ti	3.027(2)	Ti–O(20)	1.799(4)
Ti–O(30)	1.819(4)	Ti–C(1)	2.014(6)
Ti–N(1)	2.069(5)	Ti′–N(1)	2.089(5)
C(1)–N(1)	1.247(7)		
Ti–N(1)–Ti	93.4(2)	Ti–N(1)–C(1)	69.0(4)
Ti′–N(1)–C(1)	159.2 (5)	Ti–C(1)–N(1)	75.6(4)
Ti–O(20)–O(21)	159.7(4)	Ti–O(30)–C(31)	173.3(4)
O(20)–Ti–O(20)	117.3(2)		

Scheme VIII



(8) = $[(Ar''O)_2Ti(\mu\text{-}PhCN)_2Ti(OAr'')_2]$

bound to the metal center.[32] In the case of tantalum an η^2-C,N-bound pyridine was structurally characterized. Previous work by our group has shown that the fragment $[(ArO)_2Ti]$ (ArO = 2,6-diisopropylphenoxide) can bond to pyridine ligands in a normal (σ-N) fashion, although one electron reduction of one of the ligands typically occurs.[12i] Attempts to use 1 as a catalyst for production of NC_5Et_4Ph failed. The addition of PhCN to a solution of 1 containing a large excess of EtC≡CEt did not produce catalytic amounts of NC_5Et_4Ph. This appears to be due to the formation of 8 which does not react with 3-hexyne. The lack of reactivity of 8 may be due to the nature of the central core of the dinuclear unit which is discussed below.

Reactivity with Benzophenone. The titanacyclopentadiene compounds 1 and 2 undergo a ring expansion

(32) Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275.

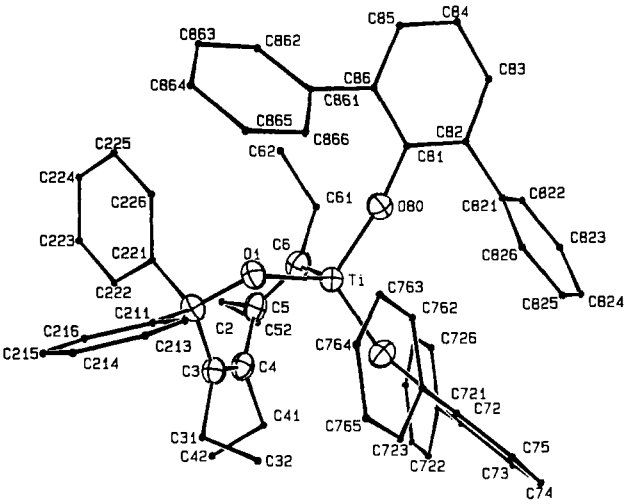


Figure 4. ORTEP view of $[(Ar''O)_2Ti(OCPh_2C_4Et_4)]$ (9).

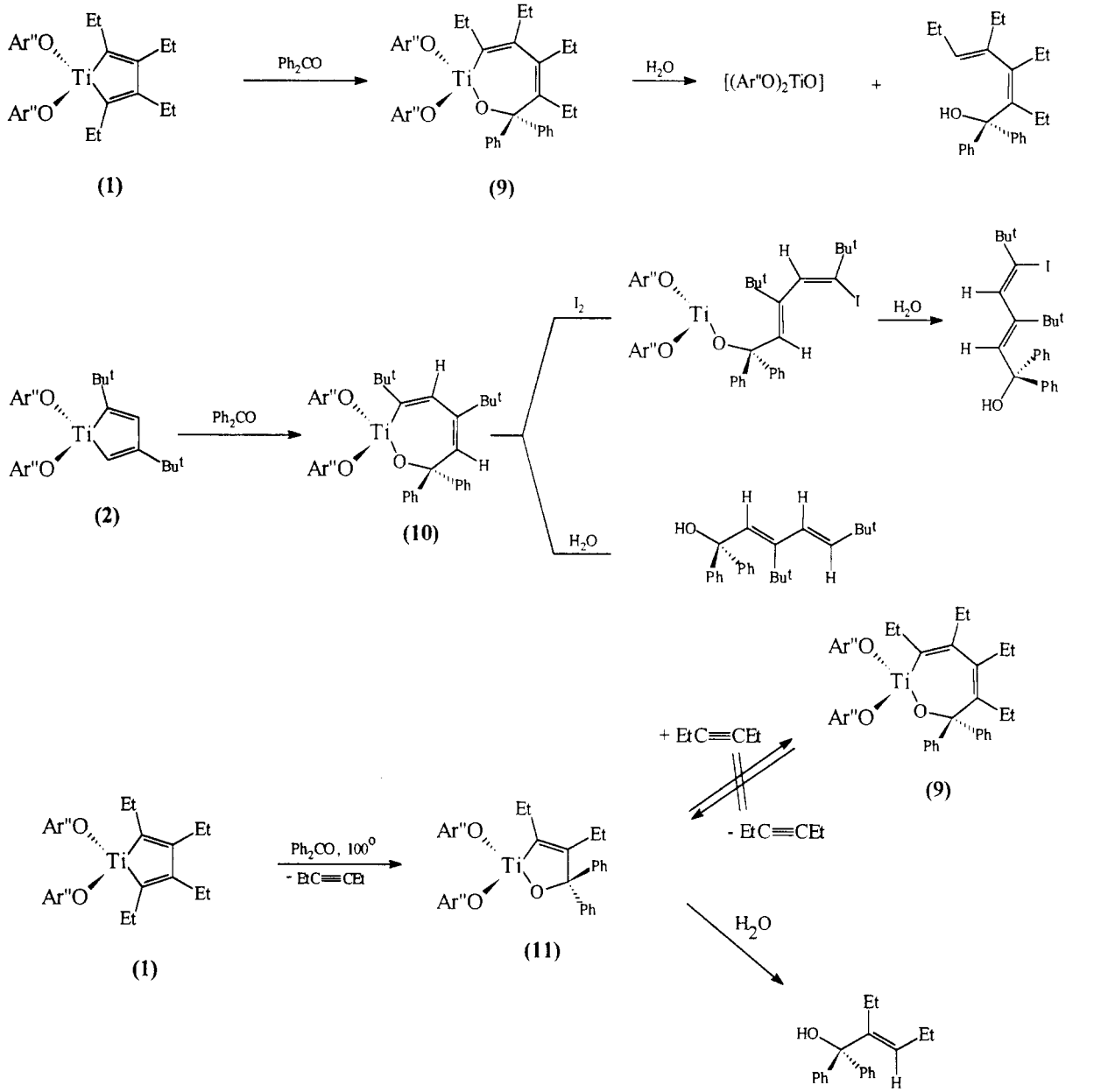
Table V. Selected Bond Distances (Å) and Angles (deg) for $[(Ar''O)_2Ti(OCPh_2C_4Et_4)]$ (9)

Ti–O(70)	1.814(1)	Ti–O(80)	1.804(1)
Ti–O(1)	1.802(1)	Ti–C(6)	2.051(2)
O(1)–C(2)	1.435(2)	C(2)–C(3)	1.555(2)
C(3)–C(4)	1.350(2)	C(4)–C(5)	1.505(2)
C(5)–C(6)	1.339(3)		
O(70)–Ti–O(80)	112.48(5)	O(1)–Ti–C(6)	99.05(6)
Ti–O(1)–C(2)	126.81(9)	Ti–O(70)–C(71)	161.0(1)
Ti–O(80)–C(81)	163.1(1)	O(1)–C(2)–C(3)	107.0(1)
C(2)–C(3)–C(4)	121.9(1)	C(3)–C(4)–C(5)	126.6(1)
C(4)–C(5)–C(6)	121.1(1)	Ti–C(6)–C(5)	112.0(1)

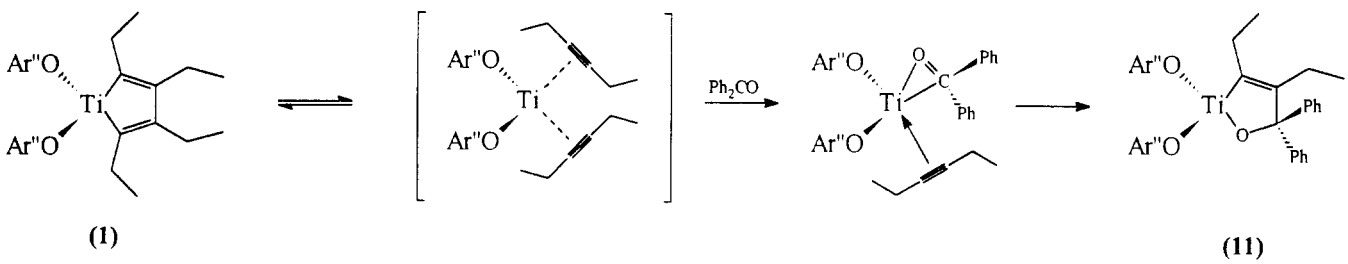
reaction with Ph_2CO at 25 °C in hydrocarbon solvents (Scheme IX). The resulting seven membered oxametallacycles 9 and 10 can be readily characterized by ^1H and ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum the carbon atom of the remaining Ti—C bond resonates at δ 210.8 and 215.8 ppm for 9 and 10, respectively. The open structure and conformation of the metallacyclic ring in 9 was confirmed by a single crystal X-ray diffraction analysis (Figure 4, Table V). The regiochemistry of 10, formed by insertion of Ph_2CO into the Ti—CH=CBu^t bond of 2, was confirmed by hydrolysis to yield the corresponding alcohol (Scheme IX). The reaction of 10 first with iodine followed by hydrolysis also yielded the corresponding iodo alcohol (Scheme IX), which was characterized by NMR and mass spectrometry.

The reaction of the tetraethyltitanacyclopentadiene compound 1 with Ph_2CO at elevated temperatures was found to lead to the 2-oxatitanacyclopent-4-ene complex 11 and 1 equiv of 3-hexyne (Scheme IX). The formation of a significant amount of 11 free from 9 required addition of Ph_2CO to a hot benzene solution of 1. Hydrolysis of 11 yielded the corresponding allylic alcohol (Scheme IX). Once formed, it was found that interconversion of 9 and 11 was not possible. The thermolysis of 9 at 100 °C in C_6D_6 in a sealed 5-mm NMR tube failed to generate 11 plus 3-hexyne. Attempts to expand the five membered metallacycle in 11 by reaction with excess 3-hexyne also failed to produce 9. It can, therefore, be concluded that these two oxametallacycles are kinetic products of the reaction of 1 with Ph_2CO. The simple ring expansion of 1 and 2 with benzophenone to produce 9 and 10 represents a special case of the typical reactivity of high valent, early d-block metal alkyl compounds toward ketonic groups. The formation of 11, however, requires intramolecular coupling of Ph_2CO with 3-hexyne. This indicates that

Scheme IX



Scheme X



there is a thermally accessible reaction pathway for 1 involving initial fragmentation of the titanacyclopentadiene ring into its component alkyne units (Scheme X). This fragmentation has been invoked for other metallacyclopentadiene complexes, e.g. to explain isomerization of nonsymmetrically substituted compounds.[24b] The fragmentation of metallacyclopentane rings into their olefin components is a general reaction[33] and occurs for the compound $[(Ar''O)_2Ti(CH_2)_4]$ on the NMR time scale.[12d]

Although the remaining titanium–carbon bond in 2-oxatitanacyclohepta-4,6-diene (9) does not react with Ph_2CO, it was found possible to elaborate the compound

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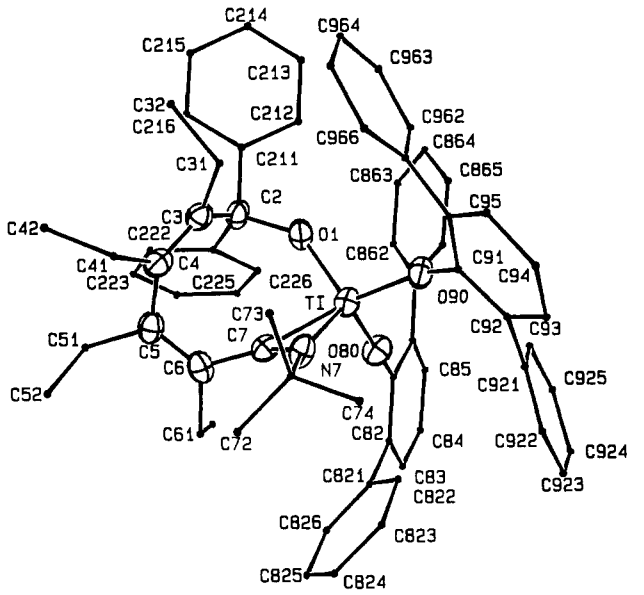
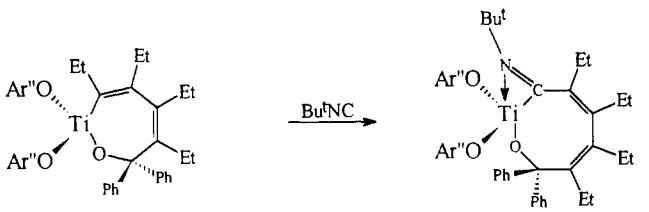


Figure 5. ORTEP view of $[(Ar''O)_2Ti(\eta^2\text{-}Bu^tNCC_4Et_4\text{-}CPh_2O)]$ (**12**).

Scheme XI



(9) (12)

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[(Ar''O)_2Ti(\eta^2\text{-}Bu^tNCC_4Et_4CPh_2O)]$ (12)

Ti–O(80)	1.818(4)	Ti–O(90)	1.896(4)
Ti–O(1)	1.805(4)	Ti–N(7)	2.040(5)
Ti–C(7)	2.026(6)	O(1)–C(2)	1.440(6)
C(2)–C(3)	1.534(8)	C(3)–C(4)	1.346(8)
C(4)–C(5)	1.497(8)	C(5)–C(6)	1.335(8)
C(6)–C(7)	1.469(8)	C(7)–N(7)	1.258(7)
O(80)–Ti–0(90)	106.2(2)	O(1)–Ti–C(7)	89.7(2)
O(1)–Ti–N(7)	110.3(2)	O(7)–Ti–N(7)	36.1(2)
Ti–O(80)–C(81)	168.9(4)	Ti–O(90)–C(91)	151.6(4)
Ti–O(1)–C(2)	142.9(3)	O(1)–C(2)–C(3)	107.2(4)
C(2)–C(3)–C(4)	127.0(5)	C(3)–C(4)–C(5)	126.7(5)
C(4)–C(5)–C(6)	119.7(5)	C(5)–C(6)–C(7)	121.6(6)
Ti–C(7)–C(6)	149.1(4)		

further by insertion of Bu^tNC into this bond to produce **12** (Scheme XI). The presence of the resulting η^2-iminoacyl group was confirmed by the presence of the characteristic $Ti(\eta^2\text{-}Bu^tNC\text{–})$ resonance at δ 240.8 ppm in the ^{13}C NMR spectrum. A single crystal X-ray diffraction analysis of **12** (Figure 5, Table VI) shows that the large metallacyclic ring can readily adopt a conformation which will allow bonding of both the nitrogen and carbon atoms of the iminoacyl group.

Discussion of the Solid State Structures. General Considerations. The five compounds subjected to single crystal X-ray diffraction analysis each contain the titanium aryloxide "unit", $[(Ar''O)_2Ti]$. Furthermore, each structure can be considered to contain a pseudotetrahedral geometry about the titanium metal center (Figures 1–5). This consideration involves viewing the η^2-C,N-bound fragments or molecules in **7**, **8**, and **12** as occupying a single site on the coordination sphere passing through the midpoint of the N–C bond.

It can be seen (Tables I–VI) that the Ar″O–Ti–OAr″ angle varies over the narrow range 106–117° for the compounds obtained in this study. This compares with values of 123.0(1) and 120.1(1)° for the simple four-coordinate molecules $[(Ar''O)_2TiPh_2]$[34] and $[(Ar''O)_2Ti(NHPh)_2]$.[35] The Ti–OAr″ distances vary from 1.788(6) Å in molecule 2 of **1** to 1.896(4) Å in **12**. These values span the range typically found for aryloxide ligands bound to Ti(IV) metal centers.[36] Similarly, the large Ti–O–Ar″ angles of 150–180° are typical. The lack of correlation between M–OAr distances and M–O–Ar angles for aryloxide compounds of the group 4 metals has been discussed.[37]

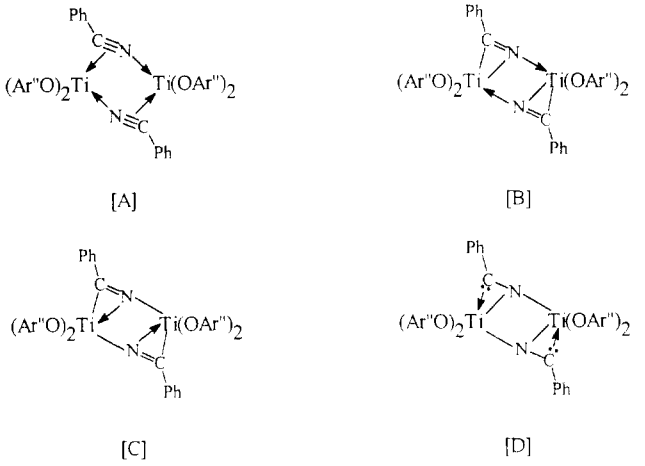
$[(Ar''O)_2Ti(C_4Et_4)]$ (1). A large number of group 4 metallocene compounds containing substituted metallacyclopentadiene rings have been structurally characterized;[16–18] cf. the complete series $[Cp_2M(C_4Ph_4)]$ (M = Ti, Zr, Hf).[16a,17a] In the aryloxide compound **1** (Figure 1, Table I) the titanium–carbon distances vary from 1.983(9) to 2.02(1) Å within the two independent molecules. This distance is much smaller than the value of 2.157(5) Å, found in $[Cp_2Ti(C_4Ph_4)]$,[16a] but very close to Ti–C(alkyl and aryl) distances in compounds such as $[(Ar''O)_3Ti(CH_2SiMe_3)]$ and $[(Ar''O)_2Ti(C_6H_5)_2]$.[34] The C_α–C_β and C_α–$C_{\beta'}$ distances of 1.32(1)–1.35(1) Å and longer C_β–$C_{\beta'}$ distances of 1.52(1) and 1.55(1) Å within the metallacycle rings of **1** are typical of metallacyclopentadiene compounds.

$[(Ar''O)_2Ti(\eta^2\text{-}Bu^tNCC_4Et_4)(py)]$ (7). The most important structural feature of this molecule concerns the bonding and orientation of the η^2-C,N-bound cyclopentadiene–imine ligand (Figure 3, Table III). Previous work by our group has led to the isolation and structural characterization of a series of η^2-imine complexes of formula $[(ArO)_2Ti(\eta^2\text{-}Bu^tNCR_2)(L)]$ (R = CH_2Ph, L = py and various 4-substituted pyridines).[31] Compound **7** is formally another example of this class of compound differing only in that the imine carbon is part of a metallacycle ring. However, there are definite differences in the bonding of the imine in **7** compared to the previously studied compounds. This is highlighted by the long Ti–C distances of 2.262(3) Å in **7** compared to values of 2.158(5) and 2.150(2) Å for L = py-4-Ph and py-4-Et in the noncyclic compounds.[31] In contrast the Ti–N distance of 1.860(2) Å in **7** is essentially identical (values of 1.846(4) and 1.855(2) Å). The elongation of the Ti–C bond in **7** is presumably due to the steric requirements of the bulky tetraethylcyclopentadiene ring. The bending away from the metal of the carbon atom of an η^2-imine ligand will eventually lead to a situation involving simple σ-N coordination of the ligand. However, the C–N distance of 1.417(3) Å in **7** can still be considered as representative of a C–N single bond (1.47 Å in amines) and is much longer than that typically found for C–N double bonds (1.28 Å in free imines).

$[(Ar''O)_2Ti(\mu\text{-}PhCN)_2Ti(OAr'')_2]$ (8). There has recently been considerable interest in the structure and

(34) Chesnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Polyhedron* **1987**, *6*, 2019.
(35) Zambrano, C. H.; Profilet, R. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron*, in press.
(36) Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1990**, *29*, 3221.
(37) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963.

Scheme XII



spectroscopy of compounds containing nitrile ligands π-bound to transition metal centers.[38] In compound **8** the molecular structure (Figure 3, Table IV) can be seen to consist of two $[(Ar''O)_2Ti]$ units held together by two benzonitrile bridging groups. There is a crystallographic inversion center which makes the two titanium atoms and two bridging groups equivalent. A description of the bonding involving each nitrile group σ-bound to one metal center and π-bound to the other would result in a formal oxidation state of +2 for the metal centers. However, the structural parameters for **8** are best accommodated into a bonding picture depicted by resonance forms C and D (Scheme XII). The two Ti–N distances of 2.069(5) and 2.089(5) Å are comparable to each other and much shorter than typical for simple dative bonds between nitrogen and titanium. The bridging ligand can be described as an N-metalated, η^2-iminoacyl group. The C–N distance of 1.247(7) Å is within the range found for η^2-iminoacyl derivatives of titanium(IV). A dizirconium compound containing a similar, unique bridging nitrile ligand has recently been reported by Hoffman et al.[39]

$[(Ar''O)_2Ti(OCPh_2C_4Et_4)]$ (9). The Ti–O and Ti–C distances within **9** are unexceptional (Figure 4, Table V). The C–C distances within the metallacycle ring clearly indicate the presence of the two double bonds: C(3)–C(4), 1.350(2) Å, and C(5)–C(6), 1.339(3) Å. The seven membered ring in **10** adopts a conformation which appears (on the basis of the internal angles) to contain very little strain at each of the constituent atoms.

$[(Ar''O)_2Ti(\eta^2\text{-}Bu^tNCC_4Et_4CPh_2O)]$ (12). As in the case of **9** above, the large metallacycle ring in **12** manages to adopt a conformation which does not appear (Figure 5, Table VI), on the basis of the angles within the ring, to contain any obvious strain. The most interesting feature of compound **12** is the bonding of the η^2-iminoacyl group. A large number of early d-block metal compounds containing η^2-iminoacyl groups are now known. A significant number of these have been subjected to single crystal X-ray diffraction analysis.[31b] One key parameter that has been discussed in detail is the value of $\Delta_{N,C} = [d(M\text{–}N) - d(M\text{–}C)]$, which gives a measure of the strength of the η^2-binding to the metal. This parameter adopts a negative value when the iminoacyl group is attached to highly electron deficient metal centers.[31b] In the case of **12** the Ti–C, Ti–N, and C–N distances are not significantly different than those found in the titanium η^2-iminoacyl compounds of formula $[(ArO)_2Ti(\eta^2\text{-}R'OCR)(R)]$.[13b] However, the value of the $\Delta_{N,C}$ parameter, +0.014, for **12** is more than the values of −0.061 and −0.081 Å found for the unchelated η^2-iminoacyl compounds. Slight elongation of the Ti–N bond over the Ti–C bond may be a consequence of the group being part of the metallacycle ring or else due to the electron deficiency of the metal being decreased by the presence of the alkoxide and two aryloxide π-donor ligands.

Experimental Section

All reactions were carried out under N_2 or vacuum using standard Schlenk techniques. Solvents were dried by distillation over Na/benzophenone under N_2. Cyclotrimerization reactions were carried out in 5-mm NMR tubes except in the case of phenylacetylene. ^1H and ^{13}C NMR spectra were recorded using a Varian Gemini 200-MHz instrument. Microanalytical and mass spectral data were acquired through Purdue in-house facilities.

Preparation of $[(Ar''O)_2Ti(C_4Et_4)]$ (1). A mixture of $[(Ar''O)_2TiCl_2]$ (2.0 g, 3.26 mmol) and 3-hexyne (0.94 mL, 8.15 mmol) in benzene (50 mL) was stirred over a sodium amalgam (0.16 g of Na, 6.95 mmol) for 12 h. The initially deep-red solution became deep-purple within 1 h and finally turned a dark-orange color. The suspension was decanted from the mercury pool, filtered, and evaporated in vacuo to yield the crude product. The crude product was redissolved in a minimum of hexane and either seeded or slowly cooled to induce the formation of orange crystals of **1**. The crystals were washed with a small amount of hexane and dried under vacuum. Anal. Calcd for $TiC_{48}H_{56}O_2$: C, 82.03; H, 6.60. Found: C, 81.43; H, 6.83. MS (EI): 702 amu (M^+). ^1H NMR (C_6D_6, 30 °C), δ: 6.9–7.5 (aromatics); 2.02 (q), 1.59 (q, CH_2Me); 0.87 (t), 0.42 (t, CH_2Me). Selected ^{13}C NMR (C_6D_6, 30 °C), δ: 231.2 (TiCEt); 160.0 (TiOC); 136.3 (TiCEtCEt); 28.4, 20.9 (CH_2Me); 14.9, 13.9 (CH_2Me). ^1H NMR (C_6D_6, 30 °C) for the partially hydrolyzed product, $[Ti(OAr'')_2(CHEtCEtCEtCEt)(OH)]$, δ: 6.9–7.5 (aromatics); 5.97 (s, OH); 5.0 (t, CHEt); 2.0 (q), 1.63 (q, CCH_2CH_3); 1.82 (pentet, $CHCH_2Me$); 0.81 (t), 0.75 (t), 0.68 (t), 0.53 (t, CH_2Me). ^1H NMR (C_6D_6, 30 °C) for the fully hydrolyzed, organic product, [CHEtCEtCEtCHEt], δ: 5.47 (t, CHEt); 2.21 (q, CCH_2Me); 2.05 ($CHCH_2Me$); 1.00 (t), 0.96 (t, CH_2Me).

Preparation of $[(Ar''O)_2Ti(C_4Bu^t{}_2H_2)]$ (2). An essentially identical procedure to that described for **1**, only using 3,3-dimethyl-1-butyne (0.80 mL, 6.50 mmol), yielded **2** as orange crystals. ^1H NMR (C_6D_6, 30 °C), δ: 6.8–7.5 (aromatics); 7.72 (d), 7.25 (d, $Ti(C_4Bu^t{}_2H_2)$, ^4J = 4.4 Hz); 1.00 (s), 0.34 (s, CMe_3). Selected ^{13}C NMR (C_6D_6, 30 °C), δ: 240.6 (TiCBu^t); 202.3 (TiCH); 160.3 (TiOC); 28.1, 29.1 (CMe_3); 37.9, 40.1 (CMe_3). ^1H NMR (C_6D_6, 30 °C) for the hydrolyzed organic product, $[Bu^tCHCHCBu^tCH_2]$, δ: 5.97 (d, Bu^{t}CH); 6.13 (dd, Bu^{t}CHCH, (*trans*) ^3J = 15.6 Hz); 5.13 (dd), 4.84 (d, CH_2, (*gem*) ^2J = 1.8 Hz); 1.01 (s), 1.10 (s, CMe_3).

Preparation of $[(Ar''O)_2Ti(C_4Me_2Ph_2)]$ (3). An essentially identical procedure to that described for **1** only using 1-phenyl-1-propyne (1.0 mL, 8.15 mmol), yielded **3** as a brown powder. ^1H NMR (C_6D_6, 30 °C), δ: 6.2–7.5 (aromatics); 1.54 (s), 1.13 (s, CMe). Selected ^{13}C NMR (C_6D_6, 30 °C), δ: 224.1, 222.6 (CMe); 160.5 (TiOC); 22.2, 19.5 (CMe). ^1H NMR (C_6D_6, 30 °C) for the partially hydrolyzed product, $[Ti(OAr'')_2(CMeCPhCMeCHPh)(OH)]$, δ: 6.8–7.5 (aromatics); 6.38 (d, CHPh, ^2J = 1.0 Hz); 5.17 (s, OH); 1.72 (d, CMeCHPh, ^2J = 1.0 Hz); 1.70 (s, TiCMe). ^1H NMR (C_6D_6, 30 °C) for the fully hydrolyzed organic product, [CHMeCPhCMeCHPh], δ: 6.8–7.8 (aromatics); 6.42 (d, CHPh, ^2J = 1.2 Hz); 5.90 (q, ^1J = 7.0 Hz, CHMe); 2.03 (d, CMe, ^2J = 1.2 Hz); 1.54 (d, ^1J = 7.0 Hz, CHMe).

Preparation of $[(Ar''O)_2Ti(C_4Ph_4)]$ (4). A mixture of $[(Ar''O)_2Ti(C_4Et_4)]$ (**1**) (0.25 g, 0.36 mmol) and diphenylacetylene

(38) (a) Barrera, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8178. (b) Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 650. (c) Anderson, S. J.; Wells, F. J.; Wilkinson, G.; Hussin, B.; Hursthouse, B. *Polyhedron* **1988**, *7*, 2615. (d) Wright, T. C.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2017. (e) Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *Organometallics* **1987**, *6*, 1073.

(39) Hoffman, D. M.; Lu, S. *Inorg. Chem.* **1992**, *31*, 2675.

Table VII. Crystal Data and Data Collection Parameters

	1	7	8	9	12
formula	$TiO_2C_{48}H_{46}$	$TiO_2N_2C_{58}H_{60}$	$Ti_2O_4N_2C_{98}H_{74}$	$TiO_3C_{68}H_{64}$	$TiO_3NC_{66}H_{65}$
fw	702.80	865.04	1439.49	977.17	968.16
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	12.627(3)	12.554(4)	23.100(4)	12.147(3)	11.774(3)
b, Å	17.378(4)	17.934(5)	12.656(3)	12.577(3)	22.775(3)
c, Å	17.739(3)	21.567(6)	27.486(7)	20.363(3)	20.137(4)
α, deg	90.41(2)			80.92(2)	
β, deg	94.68(2)	102.39(2)	109.09(2)	80.94(2)	98.320(9)
γ, deg	92.89(2)			61.78(2)	
V, Å^3	3874(3)	4742(5)	7593(6)	2694(1)	5343(3)
Z	4	4	4	2	4
d_{calc}, g cm^{-3}	1.205	1.211	1.259	1.204	1.203
cryst dimens, mm	0.44 × 0.32 × 0.25	0.44 × 0.36 × 0.09	0.38 × 0.30 × 0.25	0.52 × 0.52 × 0.50	0.31 × 0.29 × 0.20
temp, °C	20	−105	−50	−50	−20
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
monochromator	graphite	graphite	graphite	graphite	graphite
linear abs coef, cm^{-1}	2.53	2.20	2.61	2.01	2.02
abs corr applied	none	none	none	none	none
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
h,k,l limits	−13 to +13, −18 to +18, 0–18	0–13, 0–19, −23 to +22	−24 to +23, 0–13, 0–29	−12 to +13, −13 to +13, 0–21	−12 to +12, 0–24, 0–21
2θ range, deg	4.00–45.00	4.00–45.00		4.00–45.00	4.00–45.00
scan width, deg	0.83 + 0.35 tan(θ)	0.43 to 0.35 tan(θ)	0.85 + 0.35 tan(θ)	0.43 + 0.35 tan(θ)	0.66 + 0.35 tan(θ)
takeoff angle, deg	2.40	1.90	2.95	2.95	2.95
programs used	Enraf-Nonius	Enraf-Nonius	Enraf-Nonius Molen	Enraf-Nonius SDP	Enraf-Nonius SDP
F_{000}	1488.0	1840.0	3008.0	1036.0	2056.0
p factor used in weighting	0.040	6424	0.040	0.040	0.040
no. of data collcd	10 099		5220	7024	7198
no. of unique data	10 099	6424	5220	7024	7198
no. of data with $I > 3.0\sigma(I)$	3481	4739	3063	6054	3205
no. of variables	479	568	448	649	640
largest shift/esd in final cycle	0.04	0.00	0.03	0.09	0.02
R	0.075	0.040	0.060	0.039	0.047
R_w	0.080	0.055	0.074	0.056	0.052
goodness of fit	1.628	1.422	1.660	1.789	0984

(0.13 g, 0.72 mmol) in benzene (10 mL) was heated for 1 h at 110 °C. Solvent was removed under vacuum, and the residue was dissolved in benzene. Small, red crystals of **4** were obtained from benzene/hexane. Anal. Calcd for $TiC_{64}H_{46}O_2$: C, 85.89; H, 5.18. Found: C, 85.98; H, 5.40. ^{1}H NMR (C_6D_6, 30 °C), δ: 6.7–7.5 (aromatics); 6.18 (ortho TiC*Ph*). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 225.0 (TiCPh); 160.6 (TiO*C*); 145.1 (TiCPh*C*Ph).

Cyclotrimerization of Phenylacetylene. Phenylacetylene (1.00 mL, 9.1 mmol) was slowly added to a benzene solution (2 mL) of **1** (0.025 g, 0.036 mmol). The reaction mixture was eluted through a silica gel column. Solvent evaporation yielded a mixture (0.92 g) of 1,3,5-triphenylbenzene (7%) and 1,2,4-triphenylbenzene (93%). ^{1}H NMR (C_6D_6, 30 °C), δ: 7.78 (s, 1,3,5-C$_6H_3$Ph$_3$); 7.70 (d, 1,2,4-CPhCPh*CH*CPhCHCH); 7.52 (m, 1,2,4-CPhCPh-CHCPhC*H*CH); 7.40 (d, 1,2,4-CPhCPhCHCPhCHC*H*); 7.0–7.3 (m, 1,3,5- and 1,2,4-C$_6H_3$*Ph*$_3$).

Cyclotrimerization of 1-Pentyne. 1-Pentyne (0.15 mL, 1.47 mmol) was added to a benzene solution (0.5 mL) of **1** (0.030 g, 0.043 mmol). After 1 h the reaction mixture was eluted on a preparatory TLC plate. Workup yielded a mixture of 1,3,5-tripropylbenzene (28%) and 1,2,4-tripropylbenzene (72%). Selected ^{1}H NMR (C_6D_6, 30 °C), δ: 6.94–7.09 (m, 1,2,4-C$_6H_3$(C$_3$H$_7$)$_3$, ortho, ^3J = 8.3 Hz); 6.83 (s, 1,3,5-C$_6H_3$(C$_3$H$_7$)$_3$). MS (EI) for 1,3,5-tripropylbenzene: 204 (M$^+$, 24.8%), 175 amu (100.0). MS (EI) for 1,2,4-tripropylbenzene: 204 (M$^+$, 20.3%), 175 (100.0), 147 (24.4), 105 (41.7), 91 amu (21.3).

Cyclotrimerization of 1-Hexyne. 1-Hexyne (0.070 g, 0.85 mmol) was slowly added to a benzene solution (0.5 mL) of **1** (0.10 mL, 0.87 mmol). After 1 h the reaction mixture was eluted through a silica gel column. Solvent evaporation yielded a mixture of 1,3,5-tributylbenzene (31%) and 1,2,4-tributylbenzene (69%). Selected ^{1}H NMR (C_6D_6, 30 °C), δ: 6.96–7.12 (m, 1,2,4-C$_6H_3$-(C$_4$H$_9$)$_3$, ortho, J^3 = 7.7 Hz); 6.88 (s, 1,3,5-C$_6H_3$(C$_4$H$_9$)$_3$).

Cyclotrimerization of Cyclopentylacetylene. Cyclopentylacetylene (0.20 mL, 1.80 mmol) was slowly added to a benzene solution (0.50 mL) of **1** (0.050 g, 0.071 mmol). After 45 min of reaction time, a mixture of 1,3,5-tricyclopentylbenzene (30%) and 1,2,4-tricyclopentylbenzene (70%) was obtained. Selected ^{1}H NMR (C_6D_6, 30 °C), δ: 7.07–7.25 (m, 1,2,4-C$_6H_3$(C$_5$H$_9$)$_3$); 7.05 (s, 1,3,5-C$_6H_3$(C$_5$-H$_9$)$_3$); 3.32 (2 overlapping pentets), 2.92 (p, 1,2,4-C$_6H_3$(C*H*(CH$_2$)$_4$)$_3$).

Cyclotrimerization of 3-Methyl-1-butyne. An essentially identical procedure to that described for the cyclotrimerization of cyclopentylacetylene, only using 3-methyl-1-butyne (0.20 mL, 1.91 mmol), yielded a mixture of 1,3,5-triisopropylbenzene (38%) and 1,2,4-triisopropylbenzene (62%). Selected ^{1}H NMR (C_6D_6, 30 °C), δ: 7.21 (d, 1,2,4-C(Pr^i)C(Pr^i)CHC(Pr^i)CHC*H*, ortho, ^3J = 8.2 Hz); 7.06 (dd, 1,2,4-C(Pr^i)C(Pr^i)CHC(Pr^i)C*H*CH); 6.99 (s, 1,3,5-C$_6H_3$(Pr^i)$_3$); 3.17 (m), 2.81 (septet 1,2,4-C$_6$H$_3$(C*H*(Me)$_2$)$_3$); 1.25 (d, 1,3,5-C$_6$H$_3$(CHC(*Me*)$_2$)$_3$); 1.23 (d), 1.20 (d, 1,2,4-C$_6$H$_3$-(CHC(*Me*)$_2$)$_3$).

Cyclotrimerization of (Trimethylsilyl)acetylene. An essentially identical procedure to that described for the cyclotrimerization of cyclopentylacetylene, only using Me$_3$SiC≡CH (0.10 mL, 0.71 mmol), yielded 1,3,5-tris(trimethylsilyl)benzene (>95% pure by NMR). ^{1}H NMR (C_6D_6, 30 °C), δ: 7.93 (s, 1,3,5-C$_6H_3$-(SiMe$_3$)$_3$); 0.30 (s, Si(*Me*)$_3$).

Cyclotrimerization of 3,3-Dimethyl-1-butyne. 3,3-Dimethyl-1-butyne (0.14 mL, 0.85 mmol) was added to a benzene solution (0.50 mL) of **1** (0.030 g, 0.043 mmol). After 3 days of reaction time at room temperature, the reaction mixture was heated at 70 °C for a total of 22 h. This yielded 1,3,5-tris(*tert*-butyl)benzene (>95% pure by NMR). ^{1}H NMR (C_6D_6, 30 °C), δ: 7.40 (s, 1,3,5-C$_6H_3$(CMe$_3$)$_3$); 1.34 (s, 1,3,5-C$_6$H$_3$(C*Me*$_3$)$_3$).

Preparation of [(Ar″O)$_2$Ti(Bu^{t}NCC$_4$Bu$^t_2$H$_2$)] (6). *tert*-Butyl isocyanide (0.05 mL, 0.44 mmol) was added to a solution of **2** (0.20 g, 0.28 mmol) in benzene (10.50 mL). A dark-red solution of crude **6** resulted. ^{1}H NMR (C_6D_6, 30 °C), δ: 6.8–7.8 (aromatics); 6.19 (d), 4.64 (d, Bu^{t}NC$_5$Bu$^t_2$H$_2$, ^4J = 2.3 Hz); 0.78 (s, NC(*Me*)$_3$); 1.18 (s), 1.06 (s, CC(*Me*)$_3$). Selected ^{13}C NMR (C_6D_6, 30 °C), δ: 161.3 (TiO*C*); 116.5 (Bu^{t}N*C*); 67.1 (N*C*(Me)$_3$); 30.3, 32.9 (*C*C-(Me)$_3$); 32.1, 32.7, 33.9 (CC(*Me*)$_3$, NC(*Me*)$_3$).

Preparation of [(Ar″O)$_2$Ti(Bu^{t}NCC$_4$Et$_4$)] (5) and [(Ar″O)$_2$-Ti(η^2-Bu^{t}NCC$_4$Et$_4$)(py)] (7). *tert*-Butyl isocyanide (0.40 mL, 0.36 mmol) was added to a solution of **1** (0.25 g, 0.36 mmol) in 1:1 benzene/hexane. The reaction mixture was stirred for 1 h.

Removal of solvent yielded crude **5** as a noncrystalline material. Addition of pyridine (0.056 mL, 0.70 mmol) resulted in the formation of dark orange crystals of **7**. Anal. Calcd for $TiC_{58}H_{60}N_2O_2$: C, 80.53; H, 6.99; N, 3.24. Found: C, 80.29; H, 7.01; N, 3.62. ^{1}H NMR (C_6D_6, 30 °C): δ 8.51 (d, ortho *py*); 6.3–7.7 (aromatics); 1.69 (m, CH_2Me); 1.03 (t), 1.03 (t, CH_2Me); 0.64 (s, CMe_3). Selected ^{13}C NMR (C_6D_6, 30 °C), δ: 160.6 (TiO*C*); 115.2 (Bu^{t}N*C*); 65.1 (*C*Me$_3$); 31.7 (C*Me*$_3$); 19.4, 18.1 (*C*H$_2$Me$_3$); 16.5 (CH$_2$*Me*$_3$).

Preparation of [(Ar″O)$_2$Ti(OCPh$_2$C$_4$Et$_4$)] (9). Benzophenone (0.07 g, 0.36 mmol) and **1** (0.25 g, 0.36 mmol) were combined in 3:1 hexane/benzene. This resulted in the formation of yellow crystals of **9** after 12 h. Anal. Calcd for $TiO_3C_{68}H_{64}$: C, 83.16; H, 6.61. Found: C, 82.60; H, 6.86. ^{1}H NMR (C_6D_6, 30 °C), δ: 6.8–7.8 (aromatics); 5.89 (broad d, TiOC*Ph*$_2$); 1.79 (overlapping quartets), 0.99 (q), 0.11 (q, C*H*$_2$Me); 0.83 (t), 0.56 (t), 0.49 (t), 0.48 (t, CH$_2$*Me*). Selected ^{13}C NMR (C_6D_6, 30 °C), δ: 210.8 (Ti*C*Et); 161.1, 159.7 (TiO*C*); 92.2 (TiO*C*Ph$_2$); 28.0, 26.2, 24.7 (*C*H$_2$Me); 14.9, 14.5, 14.3, 13.9 (CH$_2$*Me*). ^{1}H NMR (C_6D_6, 30 °C) for the hydrolysis product, [HOCPh$_2$CEtCEtCEtCHEt], δ: 6.8–7.8 (aromatics); 4.97 (t, C*H*Et); 4.79 (s, O*H*); 1.75–2.48 (three overlapping quartets, CC*H*$_2$Me); 1.66 (p, CHC*H*$_2$Me); 1.22 (t), 0.98 (t), 0.58 (t), 0.37 (t, CH$_2$*Me*). High resolution MS calcd: 348.2453. Found: 348.2452.

Preparation of [(Ar″O)$_2$Ti(OCPh$_2$C$_4$Bu$^t_2$H$_2$)] (10). Benzophenone (0.060 g, 0.32 mmol) was added to a solution of **2** (0.010 g, 0.014 mmol) in benzene (0.060 mL). This resulted in the formation of green crystals of **10** after 48 h. ^{1}H NMR (C_6D_6, 30 °C), δ: 6.8–7.7 (aromatics); 6.68 (s, TiOCPh$_2$CHCBu^{t}C*H*CBu^t); 5.99 (s, TiOCPh$_2$C*H*CBu^{t}CHCBu^t); 0.65 (s), 0.68 (s, C*Me*$_3$). Selected ^{13}C NMR (C_6D_6, 30 °C), δ: 215.8 (Ti*C*Bu^t); 196.4 (TiCBu^t-CH*C*Bu^t); 88.1 (TiO*C*Ph$_2$); 30.5, 31.1 (CC*Me*)$_3$; 36.6, 41.0 (*C*Me)$_3$. ^{1}H NMR (C_6D_6, 30 °C) for the hydrolysis product, [HOCPh$_2$-CHCBu^{t}CHCHBu^t], δ: 6.8–7.8 (aromatics); 5.93 (dd, HOCPh$_2$-CHCBu^{t}C*H*CHBu^t, (*trans*) ^3J = 16.6 Hz, ^4J = 1.0 Hz); 5.34 (d, HOCPh$_2$CHCBu^{t}CHC*H*Bu^t); 6.33 (d, HOCPh$_2$C*H*CBu^{t}CHCH-Bu^t); 4.89 (broad s, *H*OCPh$_2$CHCBu^{t}CHCHBu^t); 0.78 (s), 1.01 (s, C*Me*$_3$).

Iodination and Hydrolysis of [(Ar″O)$_2$Ti(OCPh$_2$C$_4$-Bu$^t_2$H$_2$)] (10). Iodine (few flakes) was added to a benzene solution (0.60 mL) of **10** (0.02 g, 0.02 mmol). The reaction mixture was hydrolyzed. Workup by preparatory TLC yielded the iodo alcohol [ICBu^{t}CHCBu^{t}CHCPh$_2$OH]. ^{1}H NMR (C_6D_6, 30 °C), δ: 6.8–7.8 (aromatics); 6.63 (s), 6.75 (s, ICBu^{t}C*H*, ICBu^{t}CHCBu^{t}C*H*); 5.09 (s, O*H*); 0.96 (s), 1.13 (s, C*Me*$_3$). MS (CI): 457 ((M + H)$^+$ − H$_2$O, 79.1%), 400 (11.2), 329 (10.6), 302 (15.8), 248 amu (15.6).

Preparation of [(Ar″O)$_2$Ti(OCPh$_2$C$_2$Et$_2$)] (11). Benzophenone (0.07 g, 0.36 mmol) was combined with **1** (0.25 g, 0.36 mmol) in benzene (5 mL). This solution was rapidly heated to a high temperature while solvent was simultaneously removed under vacuum. Bright yellow crystals of **11** were obtained from benzene/hexane. Anal. Calcd for $TiC_{55}H_{46}O_3$: C, 82.28; H, 5.78. Found: C, 82.36; H, 6.02. ^{1}H NMR (C_6D_6, 30 °C), δ: 6.9–7.5 (aromatics); 1.62 (q), 1.40 (q, C*H*$_2$Me$_3$); 0.51 (t), 0.14 (t, CH$_2$*Me*$_3$). Selected ^{13}C NMR (C_6D_6, 30 °C), δ: 219.7 (Ti*C*Et); 169.1 (TiC*C*Et); 160.1 (TiO*C*); 95.8 (O*C*Ph$_2$); 26.8, 24.3 (*C*H$_2$Me$_3$); 14.5, 13.6 (CH$_2$*Me*$_3$).

Preparation of [(Ar″O)$_2$Ti(η^2-Bu^{t}NCC$_4$Et$_4$CPh$_2$O)] (12). *tert*-Butylisocyanide (32 mL, 0.28 mmol) was combined with **9** (0.25 g, 0.28 mmol) in a minimum of benzene. Yellow crystals of **12** were obtained from a benzene/hexane solution. ^{1}H NMR (C_6D_6, 30 °C), δ: 6.6–8.4 (aromatics); 2.15, 1.60, 1.15, 0.80, 0.23, −0.40 (diastereotopic multiplets, C*H*$_2$Me$_3$); 1.14 (t), 0.79 (t), 0.52 (t), 0.49 (t, CH$_2$*Me*$_3$). Selected ^{13}C NMR (C_6D_6, 30 °C), δ: 240.8 (Bu^{t}N*C*); 96.7 (TiO*C*Ph$_2$); 64.5 (*C*Me$_3$); 29.0 (C*Me*$_3$); 28.3, 25.1, 24.9, 22.5 (*C*H$_2$Me$_3$); 17.8, 16.5, 14.2, 13.6 (CH$_2$*Me*).

Crystallographic Studies. The crystal data and data collection parameters are collected in Table VII. Further details of the crystallographic studies are given in the supplementary material.

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Supplementary Material Available: Textual description of experimental procedures and full listings of the fractional coordinates, anisotropic thermal parameters, and bond lengths and angles (110 pages). Ordering information is given on any current masthead page.

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