

**SYNTHESIS AND CHARACTERIZATION OF ELECTROPHILIC
GROUP 4 METAL COMPLEXES OF BENZYNES**

By

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THESIS

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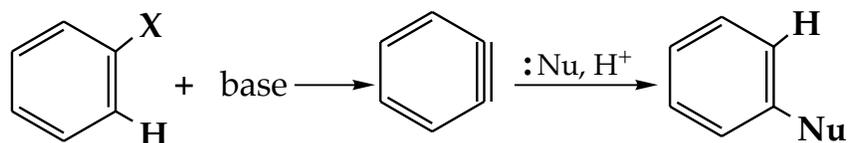
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Introduction

Benzyne

Transition metals have the ability to stabilize organic fragments that are highly reactive or unknown in the free state. Examples of these organic fragments include cyclobutadiene,¹ trimethylenemethane,² carbenes,³ small ring acetylenes,⁴ and benzyne.⁵

Benzyne, sometimes called dehydrobenzene,⁶ has not been isolated in the free state under ordinary conditions but has been observed spectroscopically in an inert matrix at very low temperatures.⁷ Benzyne exists as a highly unstable reaction intermediate in the elimination-addition mechanism for nucleophilic aromatic substitution, shown in equation 1.



(eq. 1)

There have been several representations of the bonding in benzyne. The bonding representation most generally used describes benzyne as a benzene ring with two adjacent hydrogen atoms removed. With the removal of these two hydrogen atoms, a bond in the plane of the ring is formed by the overlap of the two sp^2 orbitals, as shown in Figure 1. These two sp^2 orbitals are orthogonal to the π -molecular orbitals of the ring and are directed away from each other with reduced overlap. Unless the system departs from planarity, the interaction between these orbitals is weak, resulting in a more reactive bond.

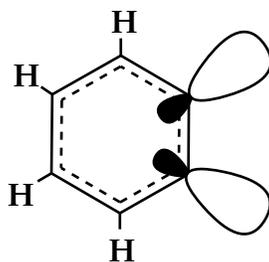
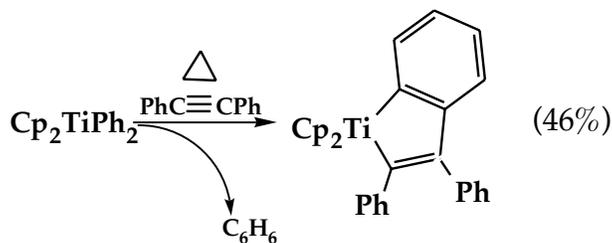


Figure 1. Diagram of benzyne.

Spectroscopic analysis gives a bond length of 1.35Å for the “triple bond” in benzyne, which is about 0.05Å shorter than the normal benzene carbon-carbon bond length.⁸

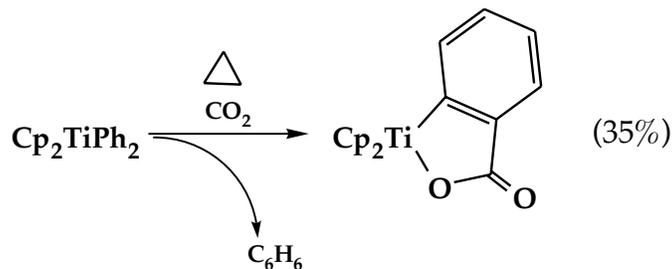
Organometallic Benzyne

As early as 1968,⁹ unusual reactivity of group 4 diarylmetallocene derivatives was noted. Refluxing diphenyltitanocene with diphenylacetylene in benzene led to a loss of a molecule of benzene and the formation of a new titanium metallacycle (eq. 2). Years later, Vol'pin¹⁰ reacted carbon dioxide



(eq. 2)

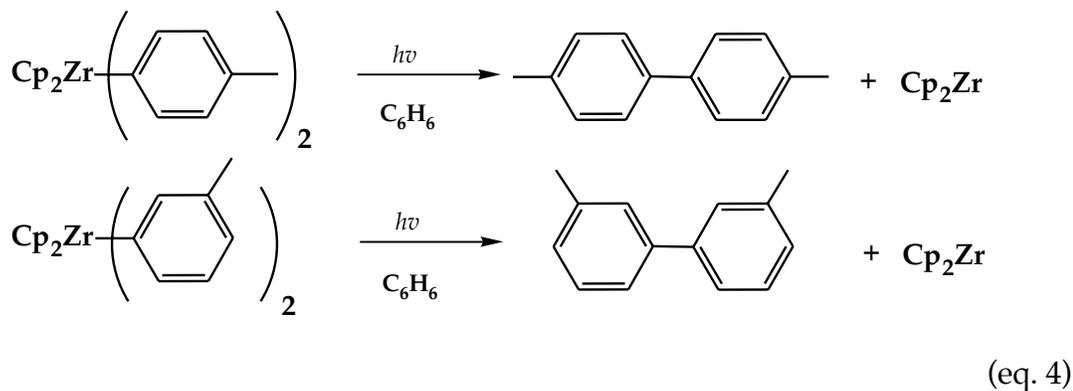
with diphenyltitanocene to form a five membered metallacycle, shown in equation 3. It was here where the titanocene-benzyne intermediate was



(eq. 3)

was proposed. Subsequent investigations by Teuben¹¹ and coworkers with deuterated compounds and solvents showed that upon thermolysis of diphenyltitanocene, deuterium labels were scrambled between the phenyl ligands, the cyclopentadienyl ligands, and the solvent. Although several studies of the thermal decomposition of alkyl- and aryl-dicyclopentadienyltitanium compounds were carried out, the nature of the mechanism of the thermolysis reaction remained uncertain.

In the late 1970's, Erker¹² and his co-workers investigated the thermal stability of diphenyl- and ditolylzirconocene derivatives and demonstrated the intermediacy of a benzyne complex. Up to this point, the hydrocarbon solvents used for the thermolysis of diphenyltitanocene and related systems were assumed to "merely act as solvents and did not participate in the reaction."¹³ Erker investigated the validity of this statement through a study of the thermolysis of diarylzirconocenes in aromatic hydrocarbon solvents. Their studies consisted of heating different diarylzirconocenes in aromatic hydrocarbon solvents and then analyzing the product mixture by photochemical degradation to form biphenyls. The photolysis did not affect the η^5 -cyclopentadienyl ligands and only selectively coupled the σ -bonded aryl groups to form biphenyls, as shown in eq. 4. Following photolysis, the biphenyls were separated using gas-liquid chromatography.



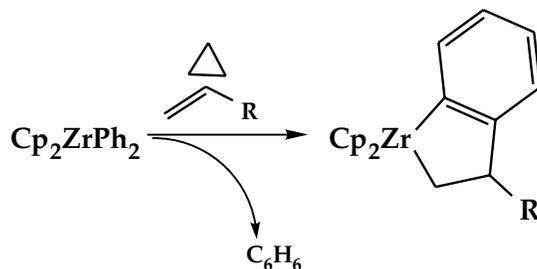
From identification of the biphenyls, the question as to whether or not the aromatic solvent interacts with diarylzirconocenes upon thermolysis could be answered.

Three separate solutions were thermalized. These solutions were di-*p*-tolylzirconocene and di-*m*-tolylzirconocene in benzene, and diphenylzirconocene in toluene. Upon heating at 70°C for ten hours followed by photochemical degradation to biphenyls, the three new diarylzirconocene structures were found to be *m*-tolylphenylzirconocene, *p*-tolylphenylzirconocene, and diphenylzirconocene.

For di-*p*-tolylzirconocene and di-*m*-tolylzirconocene, mixed tolylphenyl complexes were formed and after prolonged thermolysis, diphenylzirconocene was observed. This observation was a result of the tolyl groups being exchanged by the aromatic solvent. Alternatively, the thermolysis of diphenylzirconocene in toluene, tolyl groups from the solvent became bound to the metal and a molecule of benzene was produced as a result.

Erker concluded that upon thermolysis, the diarylzirconocenes did undergo replacement of σ -bonded ligands by aryl groups from the solvent. The fact that thermolysis of a ditolylzirconocene gave a mixture of tolylphenylzirconocenes, Erker proposed the intermediacy of an aryne complex during this exchange. It was believed that the abstraction of an ortho proton from one of the σ -bonded aryl ligands by the other aryl ligand directly led to the benzyne intermediate which then reacted with a C-H bond of the aromatic hydrocarbon.

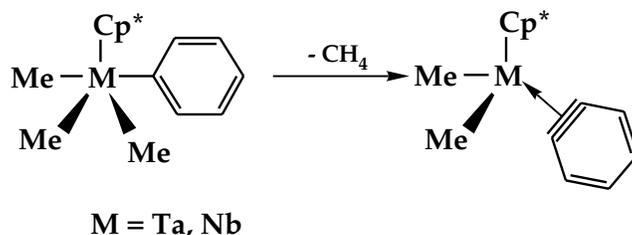
Their reactivity studies revealed that this benzyne species reductively coupled a variety of olefins to form zirconaindan derivatives¹⁴ (eq. 5). Erker and his co-workers coupled *cis*- and *trans*-stilbene to diphenylzirconocene to



(eq. 5)

form *cis*- and *trans*-metallacycles.¹⁵ This coupling of the *cis*- and *trans*-isomers was shown to be stereospecific for the formation of the respective metallacyclic products. Erker expanded his reactivity studies of the thermolysis of diarylzirconocene to coupling tungsten hexacarbonyl to afford a Fischer-type metalloxycarbene complex.¹⁶ Later, Buchwald and co-workers¹⁷ extended Erker's work to couple a variety of functional groups into a cyclohexyne and thermally generated benzyne intermediate.

Previous to 1979, transition-metal complexes containing an η^2 -benzyne group had not been isolated. Only several *o*-phenylene complexes containing the C_6H_4 unit bound to two or three transition metal atoms were known.¹⁸ Schrock and Churchill⁵ reported the first example of a benzyne ligand stabilized by complexation to a single transition-metal atom. Their development of a synthesis for tantalum-olefin complexes, $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2=\text{CHR})\text{Cl}_2$, by the decomposition of thermally unstable dialkyl complexes, $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{CH}_2\text{R})\text{Cl}_2$ ($\text{R}=\text{H}, \text{Me}$) led to the preparation of stable benzyne complexes (eq. 6).



(eq. 6)

The syntheses of these monomeric niobium- and tantalum-benzyne complexes were based on the fact that many transition metal aryl complexes decompose through a form of β -hydride elimination.¹⁹

The molecular geometry of the tantalum analogue was determined by means of single-crystal X-ray structural analysis. This structural analysis revealed that the benzyne ligand plane was oriented perpendicular to the plane of the cyclopentadienyl system. The orientation of the benzyne ligand

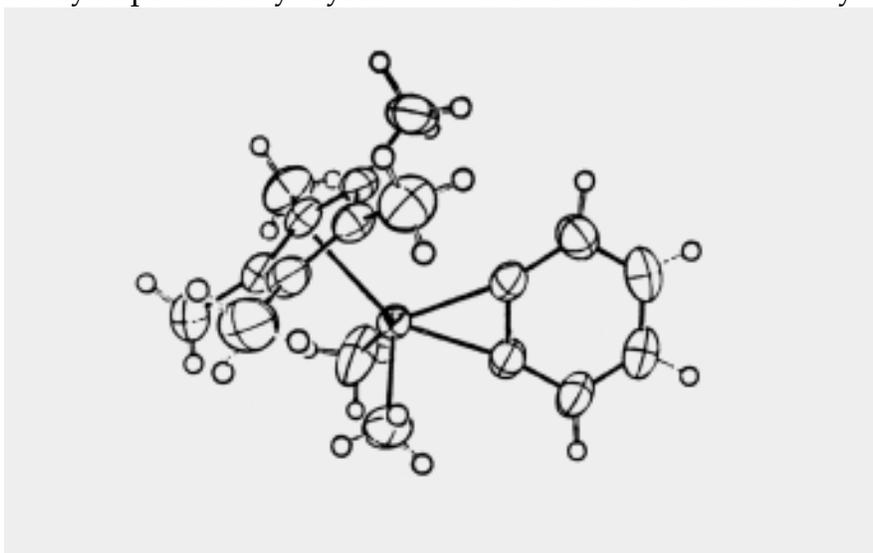
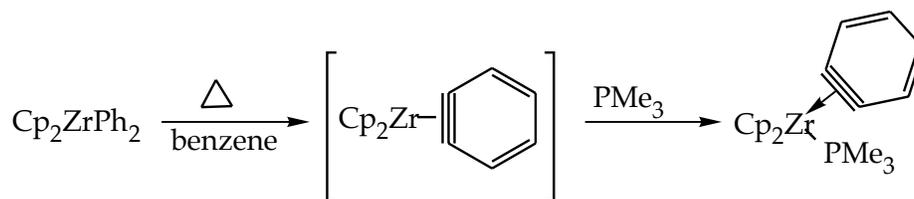


Figure 2. Molecular structure of Ta(n⁵-C₅Me₅)(C₆H₄)Me₂.

allowed maximum overlap of the benzyne's π orbitals with both empty σ -acceptor and π -acceptor orbitals on the electron deficient metal atom. This geometric orientation resulted in stabilization of the complex.

Buchwald and co-workers subsequently prepared a zirconocene-benzyne intermediate. This was accomplished by heating a benzene solution of diphenylzirconocene in the presence of a large excess of trimethylphosphine,²⁰ shown in equation 7. The trimethylphosphine adduct of the zirconocene-benzyne complex was isolated and its X-ray crystal structure was determined. An examination of the structural data revealed



(eq. 7)

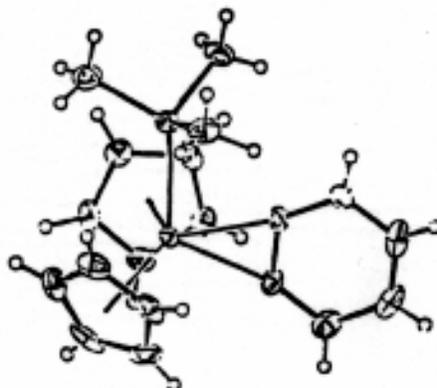
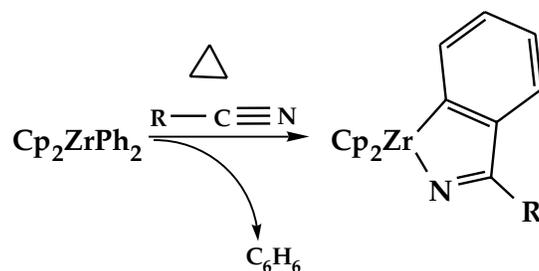


Figure 3. Molecular structure of trimethylphosphine adduct of the zirconocene-benzyne complex.

that the benzyne moiety experienced little strain, with the “triple bond” length and angles at the two carbon atoms varying only slightly from that seen in benzene. This adduct would prove useful as it would undergo clean, high yield reactions upon treatment of a number of reagents including ketones and nitriles,¹⁶ unlike that the corresponding in situ generated benzyne intermediate.

Buchwald and co-workers²¹ coupled the thermally-generated benzyne from diphenylzirconocene with a wide variety of nitriles to produce a series of azazirconacyclopentadienes, shown in equation 8. This coupling reaction



(eq. 8)

would prove useful as a means for carbon-carbon bond formation leading to conversion of the metallacyclic products obtained into a variety of organic reagents suitable for synthetic purposes.

Modified Metallocene Systems

Although the reactivity of group 4 metallocene benzyne has been extensively examined, far less is known about the influence of the electrophilicity of the metal center on the reactivity of coordinated benzyne. Recently, Bercaw and co-workers²² demonstrated that the replacement of the two cyclopentadienyl rings with the dianionic bifunctional chelating ligand $[(\text{C}_5\text{Me}_4)\text{SiMe}_2(\text{N}-t\text{-Bu})]^{2-}$ provides an effective means for enhancing the Lewis acidity of d^0 scandium complexes. The weaker π -donating character and lower steric requirement of the amido functionality enhances the metal's Lewis acidity by the simultaneous reduction of the formal electron count and the steric crowding at the metal center. The electron count is reduced by two, bringing the electron count to 14 electrons for the *ansa*-monocyclopentadienyl amido scandium complex, compared to 16 electrons for the corresponding scandocene complexes. Researchers at Dow Chemical Co.²³ and Exxon²⁴ later extended Bercaw's findings and attached *ansa*-monocyclopentadienyl ligands to group 4 metals to give complexes of the general formula,

$[(C_5R_4)SiR'_2(NR'')]MCl_2$, where $M=Ti, Zr, Hf$; $R=alkyl$; $R', R''=alkyl, aryl$. They demonstrated that when these compounds are activated with methylalumoxane, the resultant species behaves as a highly active Ziegler-Natta catalyst for the copolymerization of ethylene and 1-alkenes or styrene. This new ligand system offers a means of increasing the electrophilicity and decreasing the steric crowding at an electrophilic group 4 metal center.

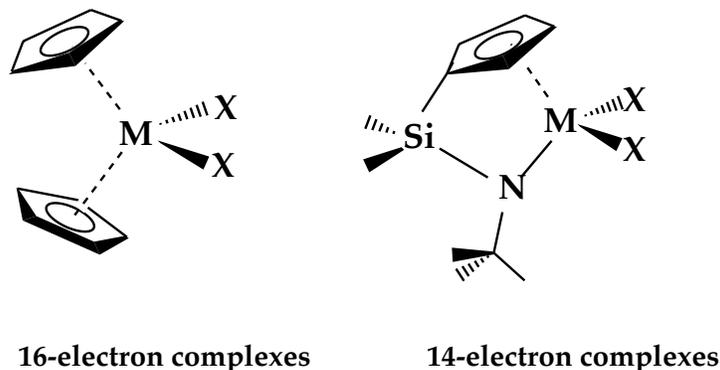
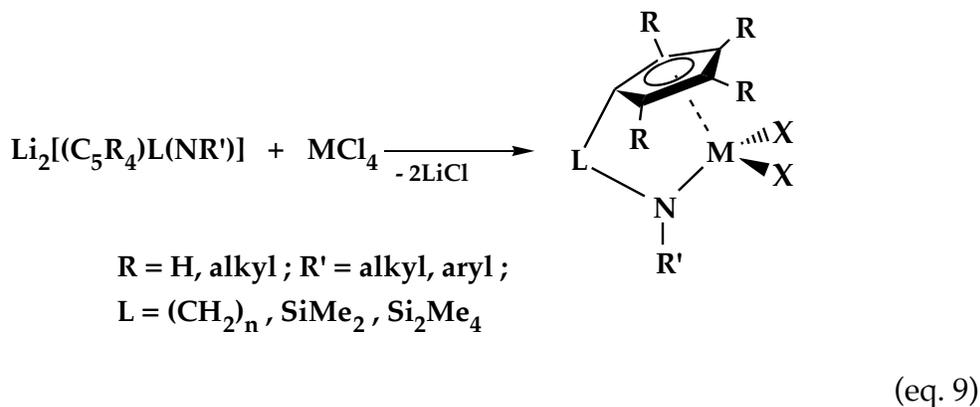


Figure 4. Structures of group 4 metallocene and *ansa*-monocyclopentadienyl amido metal complexes.

The molecular structures for these modified metallocene complexes indicate that the ligands similarly adopt a pseudo-tetrahedral arrangement around the metal center. With the presence of the dimethylsilyl bridge, the $Cp(c)-M-N$ bite angle is $25-30^\circ$ smaller than the $Cp(c)-M-Cp(c)$ angle of $125-135^\circ$ in the corresponding 16-electron metallocene systems. The ligand modification coupled with the availability of an additional vacant metal orbital now offers a new perspective into the reactivity associated with group 4 metallocenes. In addition, the steric and electronic features of the ligand may be varied by changing the substituents on the cyclopentadienyl and/or amido functionalities and also by using a different moiety to link the cyclopentadienyl ring to the amido group.

Two primary synthetic strategies have been developed for the synthesis of *ansa*-monocyclopentadienyl amido complexes: *metathesis* and *amine*

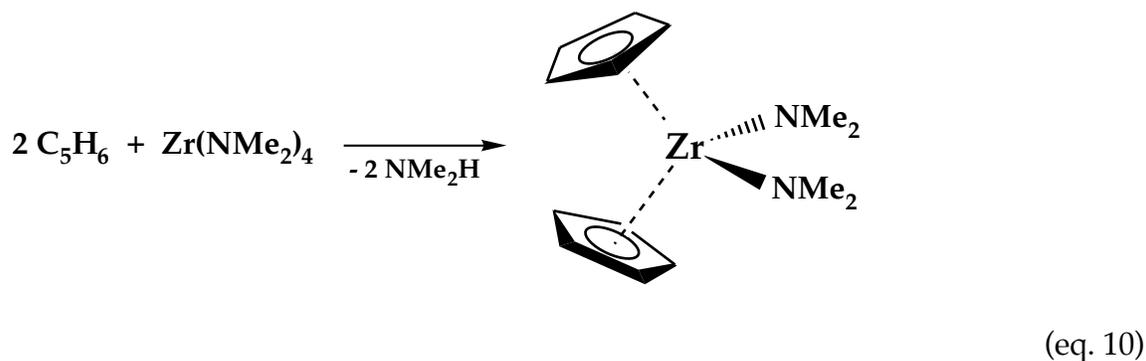
elimination. As mentioned earlier, Bercaw's group, along with researchers at Dow Chemical Co. and Exxon, relied on the metathetical reaction of the appropriate dilithio salt or diGrignard reagent of $[(C_5R_4)L(NR')]^{2-}$ with a metal chloride to chelate the *ansa*-monocyclopentadienyl amido ligand to the electrophilic metal center (eq. 9). Okuda and co-workers²⁵ used the same



approach for the preparation of various *ansa*-monocyclopentadienyl Ti and *ansa*-monofluorenyl amido Zr compounds. Unfortunately, the metathesis route in some cases led to low isolated yields and mixtures of products.

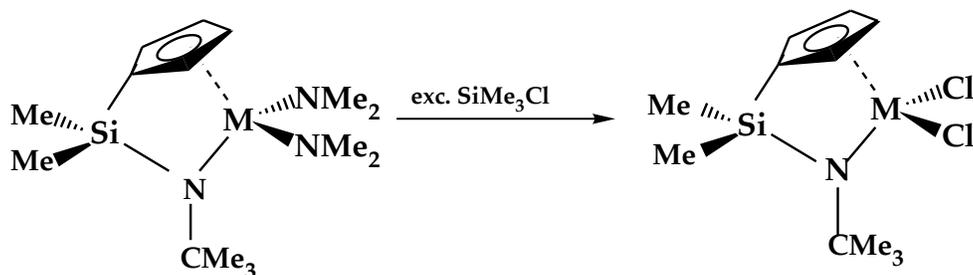
The alternative amine elimination strategy is based on Lappert's earlier observation for the preparation of group 4 metallocenes, shown in eq. 10.²⁶ The reaction of Zr(NMe₂)₄ with excess cyclopentadiene produces (C₅H₅)₂Zr(NMe₂)₂ and releases two equivalents of NMe₂H. Teuben and co-workers²⁷ later adapted this strategy for the synthesis of *ansa*-monocyclopentadienyl amido group 4 complexes that featured a three-carbon

linkage. The reactions of $[\text{C}_5\text{H}_5(\text{CH}_2)_3\text{NHMe}]$ with $\text{M}(\text{NMe}_2)_4$ ($\text{M}=\text{Zr}, \text{Hf}$)



produced $[(\text{C}_5\text{H}_4)\text{CH}_2\text{CH}_2\text{CH}_2(\text{NCH}_3)]\text{M}(\text{NMe}_2)_2$ in good yields (94% for $\text{M}=\text{Zr}$, 58% for $\text{M}=\text{Hf}$). Because of the greater utility of halide derivatives for the preparation of other organometallic compounds, the bis(dimethylamido) derivatives were converted to their dihalide amine adduct $[(\text{C}_5\text{H}_4)\text{CH}_2\text{CH}_2\text{CH}_2(\text{NCH}_3)]\text{MX}_2(\text{NMe}_2\text{H})$, ($\text{M}=\text{Zr}, \text{Hf}$; $\text{X}=\text{Cl}, \text{I}$), by the stoichiometric addition of 2 equivalents of dimethylamine hydrohalide ($\text{NMe}_2\text{H}\cdot\text{HCl}$ or $\text{NMe}_2\text{H}\cdot\text{HI}$). Teuben and co-workers were able to synthesize a series of $[(\text{C}_5\text{H}_4)\text{CH}_2\text{CH}_2\text{CH}_2(\text{NCH}_3)]\text{ZrR}_2$ complexes, where ($\text{R}=\text{CH}_2\text{C}_6\text{H}_5$, CH_2SiMe_3 , BH_4), and $\{[(\text{C}_5\text{H}_4)\text{CH}_2\text{CH}_2\text{CH}_2(\text{NCH}_3)]\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)(\mu\text{-Cl})\}_2$. The range of *ansa*-monocyclopentadienyl amido group 4 metal complexes that can be prepared by the amine elimination route was extended by Herrmann and co-workers,²⁸ who prepared a series of half-sandwich related compounds featuring a dimethylsilyl bridge between a cyclopentadienyl ring or indenyl group. Petersen and co-workers²⁹ observed that the thermally-induced amine elimination reaction from 1:1 neat mixtures of $\text{M}(\text{NMe}_2)_4$ and $[(\text{C}_5\text{H}_5)\text{SiMe}_2(\text{N}(\text{H})\text{-t-Bu})]$ under a modest N_2 purge at $110\text{-}120^\circ\text{C}$ affords $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{M}(\text{NMe}_2)_2$ ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$), and $[(\text{C}_{13}\text{H}_8)\text{SiMe}_2(\text{N-t-Bu})]\text{Zr}(\text{NMe}_2)_2$.²⁸ A modified approach was subsequently used to prepare $[(\text{C}_9\text{H}_6)\text{SiMe}_2(\text{N-t-Bu})]\text{M}(\text{NMe}_2)_2$ ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$) and $[(\text{C}_{13}\text{H}_8)\text{SiMe}_2(\text{N-t-$

Bu)]Zr(NMe₂)₂.³⁰ The conversion of these dimethylamido complexes to the corresponding dichloride derivatives was accomplished by the addition of two equivalents of SiMe₃Cl, shown in eq. 11. The volatile silylamine by-product is readily removed under reduced pressure.



(eq. 11)

Research Objectives

Early transition metal complexes, such as [(C₅R₄)SiMe₂(N-t-Bu)]ML₂ where M is a d⁰ group 4 metal, that contain a bifunctional monocyclopentadienyl ligand represent an emerging class of organometallic complexes with enormous chemical potential. Because of the availability of reliable, high yield syntheses of [(C₅Me₄)SiMe₂(N-t-Bu)]ZrCl₂ and [(C₅H₄)SiMe₂(N-t-Bu)]TiCl₂, a research effort was taken to prepare the corresponding diphenyl derivatives and investigate their reactivity toward unsaturated organic substrates upon thermolysis. The substrate chosen for the investigation of trapping the reactive benzyne intermediate was diphenylacetylene. Examination of the products obtained will provide the opportunity to evaluate the stereoelectronic consequences of this alternative *ansa*-metallocene ligand system on the structure and reactivity and thus differentiate their chemical reactivity from the corresponding group 4

metallocene benzyne complexes. This new class of organometallic compounds may lead to the development of new chemical application for selective transformations in organic synthesis as well as the possible chemical potential for the generation of structures not accessible via metallocene benzyne species.

Experimental Section

Reagents

Reagent grade hydrocarbon and etheral solvents were purified using standard methods³¹ and distilled under nitrogen. These solvents were then transferred to storage flasks containing either $[(C_5H_5)_2Ti(\mu-Cl)_2]_2 Zn$ ³² or potassium benzophenone ketyl. Hexamethyldisiloxane was dried over $(C_5H_5)_2ZrMe_2$. The deuterated solvents, C_6D_6 (Cambridge Isotopes, 99.5%) and $CDCl_3$ (Aldrich, 99.8%) were dried over activated 4A molecular sieves prior to use, as was NH_2-t-Bu (Acros).

Starting materials such as $TiCl_4(THF)_2$,³³ $NaCp$,³⁴ and LiC_5Me_4H ³⁵ were prepared by literature procedures. Other starting materials such as $TiCl_4$ (Aldrich), $ZrCl_4$ (Alfa), $LiNMe_2$ (Aldrich 95%), Na (Aldrich), $C_5Me_4H_2$ (Boulder Scientific), dicyclopentadiene (Kodak), phenyllithium (Aldrich), phenylmagnesiumbromide (Aldrich), and phenylmagnesiumchloride (Acros) were used without further purification, whereas diphenylacetylene (Kodak) was purified by sublimation. $SiMe_2Cl_2$ (Acros) and $SiMe_3Cl$ (Acros) were vacuum distilled prior to use.

Instrumentation

The 1H and ^{13}C NMR spectra were measured with either a JEOL GX-270 or a JEOL Eclipse 270 NMR spectrometer operating in the FT mode at 270 MHz (1H) or 67.5 MHz (^{13}C). The 1H chemical shifts are referenced to the residual proton peaks of benzene- d_6 at δ 7.15 (vs. TMS) or chloroform- d_1 at δ 7.24 (vs. TMS). The ^{13}C resonances are referenced to the central peak of benzene- d_6 at δ 128.0 (vs. TMS) or chloroform- d_1 at δ 77.0 (vs. TMS).

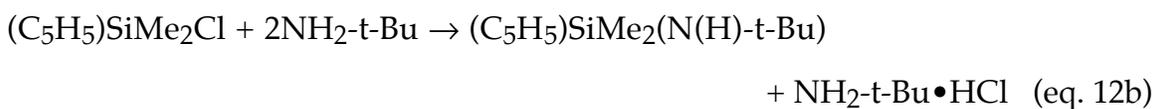
General Procedures

To minimize exposure to air and moisture during the syntheses of compounds, all manipulations and reactions were carried out on a high-vacuum line or in a Vacuum Atmosphere glovebox equipped with a HE-493 Dri-Train. Reactions were typically carried out in pressure equalizing filter-frits equipped with high vacuum Teflon stopcocks. All glassware were oven-dried and flame-dried under vacuum prior to use. NMR sample tubes were sealed normally under 400-500 Torr of nitrogen. Nitrogen was purified by passage over reduced BTS catalysts and activated 4A molecular sieves. Elemental analyses were performed by E&R Microanalytical Labs, Parsippany, NJ 07054.

Syntheses of Compounds

Preparation of $(C_5H_5)SiMe_2(N(H)-t-Bu)$

The preparation of $(C_5H_5)SiMe_2(N(H)-t-Bu)$ was accomplished in two separate steps, as shown in eq. 12. This compound was then used directly in an amine elimination reaction to afford the *ansa*-monocyclopentadienyl amido metal complex.



(a) Preparation of chlorocyclopentadienyldimethylsilane, $(C_5H_5)SiMe_2Cl$

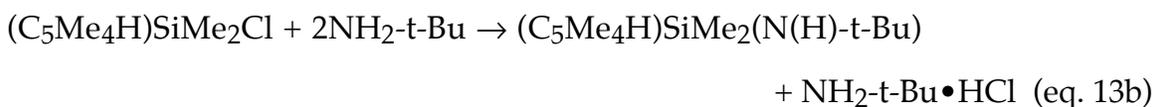
A 6.00g sample (68.1 mmol) of NaC_5H_5 was added to an addition sidearm, which was then attached to a 250 mL three-neck flask. After connecting the reaction flask to a filter frit assembly, the third neck was capped and the assembly was evacuated. Diethyl ether (*ca.* 150 mL) and 33.0 mL (272.5 mmol) of $SiMe_2Cl_2$ were introduced by vacuum distillation. The reaction mixture was cooled in a liquid $N_2/2$ -propanol bath and stirred while the NaC_5H_5 was added incrementally over a two hour period. Upon completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was filtered and the solvent and excess $SiMe_2Cl_2$ were removed by vacuum distillation while the flask containing the mixture was kept at $0^\circ C$, leaving 6.85 g (63.3% yield) of product as a light yellow oil.

(b) Preparation of tert-butylaminocyclopentadienyldimethylsilane, $(C_5H_5)SiMe_2(N(H)-t-Bu)$

All of the $(C_5H_5)SiMe_2Cl$ (6.85 g, 43.19 mmol) isolated from the preceding reaction was added to a 200 mL round bottom flask which was then attached to a filter frit assembly. THF (*ca.* 100 mL) and 9.06 mL NH_2-t-Bu (86.3 mmol) were added to the reaction flask via vacuum distillation. A white precipitate of $NH_2-t-Bu \bullet HCl$ formed while the reaction was stirred for three days. The solution was filtered and the solvent was removed under reduced pressure to give 6.07 g (71.9% yield) of product as a yellow oil. The 1H NMR spectrum contains three separate sets of resonance for the methyl groups of the t-butyl and the dimethylsilyl linkage consistent with the presence of three cyclopentadiene isomers.²⁷

Preparation of $(C_5Me_4H)SiMe_2(N(H)-t-Bu)$

The preparation of $(C_5Me_4H)SiMe_2(N(H)-t-Bu)$ was also accomplished in two separate steps, as shown in eq. 13. This compound was then used directly in an amine elimination reaction to afford the *ansa*-monotetramethylcyclopentadienyl amido metal complex.



(a) Preparation of chloromethylcyclopentadienyldimethylsilane,

$(C_5Me_4H)SiMe_2Cl$

A 2.44 g sample (19.0 mmol) of LiC_5Me_4H was placed in a 200 mL Solv-seal flask. Approximately 40 mL of THF and 7.7 mL (63.4 mmol) of $SiMe_2Cl_2$ were added by vacuum distillation. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The solvent and excess $SiMe_2Cl_2$ were removed under vacuum and were replaced by an equal amount of pentane. After filtration, the pentane was removed, leaving 3.75 g (91.5% yield) of $(C_5Me_4H)SiMe_2Cl$ as a light yellow oil.

(b) Preparation of tert-butylaminotetramethylcyclopentadienyldimethylsilane,

$(C_5Me_4H)SiMe_2(N(H)-t-Bu)$

The $(C_5Me_4H)SiMe_2Cl$ (3.75 g, 17.4 mmol) was transferred to another frit assembly. THF (ca. 50 mL) and 4.6 mL (43.8 mmol) of NH_2-t-Bu were then added. The mixture was allowed to warm to room temperature and stirred

for three days. After removal of solvent, the product was extracted with pentane (ca. 30 mL) yielding 3.52 g (80.2%) of $(C_5Me_4H)SiMe_2(N(H)-t-Bu)$ as a light yellow oil.

Synthesis of $M(NMe_2)_4$, $M= Ti, Zr$.

(a) Preparation of $Ti(NMe_2)_4$

A 5.13 g sample (15.3 mmol) of $TiCl_4(THF)_2$ was placed in an addition sidearm and connected to a two-neck flask containing 3.14 g (61.6 mmol) of $LiNMe_2$. Toluene (ca. 50 mL) was added via vacuum transfer and the flask was then cooled in a liquid $N_2/2$ -propanol bath. The $TiCl_4(THF)_2$ was slowly added to the stirring reaction mixture. The mixture was stirred overnight at room temperature. The solution was then filtered and the toluene was removed under reduced pressure. Removal of toluene left 3.03 g (87.8% yield) of $Ti(NMe_2)_4$ as a yellow oil.

(b) Preparation of $Zr(NMe_2)_4$

A 6.00 g sample (25.7 mmol) of $ZrCl_4$ was placed in an addition sidearm and connected to a two-neck flask containing 5.66 g (110.9 mmol) of $LiNMe_2$. Toluene (ca. 125 mL) was added via vacuum transfer and the $ZrCl_4$ was added to the reaction mixture over a one hour period. The reaction was stirred overnight. The solution was then filtered and the toluene was removed under reduced pressure. The product was purified by sublimation at $40^\circ C$ and 10^{-4} Torr affording 4.49 g (65.2% yield) of $Zr(NMe_2)_4$ as a light yellow semicrystalline solid.

**Synthesis of $[(C_5R_4)SiMe_2(N-t-Bu)]M(NMe_2)_2$, $R=H, Me$; $M=Ti, Zr$
via Amine Elimination**

(a) Preparation of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(NMe_2)_2$

A 1.96 g sample (8.74 mmol) of $Ti(NMe_2)_4$ was combined with 1.71g (8.75 mmol) of $(C_5H_5)SiMe_2(N(H)-t-Bu)$ in a 100 mL pear-shaped flask equipped with a vacuum adapter. The neat reaction mixture was heated to 120°C and stirred overnight under a modest N_2 purge. During the course of the reaction, an orange solid, $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(NMe_2)_2$, collected on the walls of the reaction flask. Following the evacuation of volatiles, sublimation of the product at 40°C and 10^{-4} Torr gave 2.21 g (76.7% yield) of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(NMe_2)_2$ as a semicrystalline solid. 1H NMR (C_6D_6 , $^3J_{HH}$ in Hz): δ 6.25, 5.99 (C_5H_4 , t, 2.3), 2.95 (NMe_2 , s), 1.31 ($NCMe_3$, s), 0.51 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR (C_6D_6 , $^1J_{CH}$ in Hz): δ 117.9, 116.3 (proximal and distal carbons of C_5H_4 , d, 169), 107 (bridgehead C, s), 59.6 ($NCMe_3$, s), 49.6 (NMe_2 , q, 133), 34.0 ($NCMe_3$, q, 124), 1.7 ($SiMe_2$, q, 119).

(b) Preparation of $[(C_5H_4)SiMe_2(N-t-Bu)]Zr(NMe_2)_2$

A 3.00 g sample (11.2 mmol) of $Zr(NMe_2)_2$ was combined with 2.19 g (11.2 mmol) of $(C_5H_5)SiMe_2(N(H)-t-Bu)$ in a 100 mL pear-shaped flask equipped with a high vacuum adapter. The neat reaction mixture was heated to 120°C and stirred for two days. The volatile NMe_2H was removed by a slow purge of N_2 and periodic evacuation of the reaction mixture. As the reaction proceeded, a light yellow solid formed on the walls of the flask. Following evacuation of volatiles, the product was collected via sublimation at 40°C and 10^{-4} Torr, giving 2.56g (61.2% yield) of $[(C_5H_4)SiMe_2(N-t-Bu)]Zr(NMe_2)_2$ as a light yellow waxy solid. 1H NMR (C_6D_6 , $^3J_{HH}$ in Hz):

δ 6.31, 6.18 (C_5H_4 , t, 2.4), 2.80 (NMe_2 , s), 1.28 ($NCMe_3$, s), 0.55 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR (C_6D_6 , $^1J_{CH}$ in Hz): δ 118.4, 114.8 (proximal and distal carbons of C_5H_4 , d, 169), 108.3 (bridgehead carbon, s), 55.9 ($NCMe_3$, s), 44.0 (NMe_2 , q, 132), 34.5 ($NCMe_3$, q, 124), 2.34 ($SiMe_2$, q, 117).

(c) Preparation of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(NMe_2)_2$

A 2.41 g sample (9.00 mmol) of $Zr(NMe_2)_4$ was combined with 2.26 g (8.98 mmol) of $(C_5Me_4H)SiMe_2(N(H)-t-Bu)$ and toluene (*ca.* 3 mL) in a 100 mL pear-shaped flask equipped with a vacuum adapter. The reaction mixture was heated to 110°C and stirred 24 hours under a modest N_2 purge. As the reaction proceeded, solid formed on the walls of the reaction flask. The toluene was removed under reduced pressure and the product was purified by sublimation at 60°C and 10^{-4} Torr to give 3.60 g (93.5% yield) of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(NMe_2)_2$ as an off-white solid. 1H NMR (C_6D_6): δ 2.84 (NMe_2 , s), 2.14, 1.90 (C_5Me_4 , s), 1.33 ($NCMe_3$), 0.65 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR (C_6D_6 , $^1J_{CH}$ in Hz): δ 127.4, 124.6 (proximal and distal carbons of C_5Me_4 , s), 100.9 (bridgehead C, s), 56.0 ($NCMe_3$, s), 44.5 (NMe_2 , q, 136), 34.6 ($NCMe_3$, q, 125), 14.0, 11.1 (C_5Me_4 , q, 128), 7.44 ($SiMe_2$, q, 120).

Conversion of $[(C_5R_4)SiMe_2(N-t-Bu)]M(NMe_2)_2$, (R=H, Me; M=Ti, Zr), to $[(C_5R_4)SiMe_2(N-t-Bu)]MCl_2$.

(a) Synthesis of $[(C_5H_4)SiMe_2(N-t-Bu)]TiCl_2$

A 2.48 g sample (7.52 mmol) of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(NMe_2)_2$ was dissolved in *ca.* 5 mL toluene. $SiMe_3Cl$ (2.1 mL, 16.5 mmol) was added by vacuum transfer, and the reaction mixture was stirred 24h at 65°C. As the reaction proceeded, the original reddish brown color of the solution became

dark and then turned orange once the reaction was complete. After removal of the volatiles, the procedure was repeated one more time to ensure complete conversion. A sublimator was then attached and 2.22 g (94.4% yield) of $[(C_5H_4)SiMe_2(N-t-Bu)]TiCl_2$ as an orange solid was collected by sublimation at 50-60°C and 10^{-4} Torr. 1H NMR (C_6D_6 , $^3J_{HH}$ in Hz): δ 6.60, 6.07 (C_5H_4 , t, 2.3), 1.38 ($NCMe_3$, s), 0.18 ($SiMe_2$, s); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 126.3, 125.6 (proximal and distal carbons of C_5H_4), 110.0 (bridgehead C), 63.7 ($NCMe_3$), 32.2 ($NCMe_3$), -0.20 ($SiMe_2$).

(b) Synthesis of $[(C_5H_4)SiMe_2(N-t-Bu)]ZrCl(\mu-Cl)_2$

A 2.52 g sample (6.76 mmol) was placed in a 100 mL pear-shaped flask. Toluene (*ca.* 25 mL) and 1.72 mL (13.5 mmol) of $SiMe_3Cl$ were added via vacuum distillation. The reaction mixture was stirred 24h at 65°C. The solvent was removed under reduced pressure. The remaining solid was washed with pentane (*ca.* 20 mL) to remove soluble impurities. The product was dried under reduced pressure leaving 2.18g (90.9% yield) of $[(C_5H_4)SiMe_2(N-t-Bu)]ZrCl(\mu-Cl)_2$ as a dry, off-white solid. 1H NMR ($CDCl_3$, $^3J_{HH}$ in Hz): δ 6.91, 6.44 (C_5H_4 , t, 2.3), 1.38 ($NCMe_3$, s), 0.54 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR ($CDCl_3$, $^1J_{CH}$ in Hz): δ 122.1, 121.2 (proximal and distal carbons of C_5H_4 , d, 174), 109.8 (bridgehead carbon, s), 57.7 ($NCMe_3$, s), 32.6 ($NCMe_3$, q, 125), 0.90 ($SiMe_2$, q, 120).

(c) Synthesis of $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrCl_2$

A 6.98 g sample (16.2 mmol) of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(NMe_2)_2$ was placed in a 100 mL round bottom flask. Approximately 25 mL of toluene and 5 mL (39.3 mmol) of $SiMe_3Cl$ were added by vacuum distillation. The reaction mixture was stirred 24h at 60°C. The solvent was then removed

from the resulting yellow reaction mixture. After removal of solvent, the remaining solid was washed with approximately 20 mL pentane, leaving 6.15g (92% yield) of $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrCl_2$ as a dry off-white solid. 1H NMR ($CDCl_3$): δ 2.18, 2.12(C_5Me_4 , s), 1.39 ($NCMe_3$, s), 0.61 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR ($CDCl_3$, $^1J_{CH}$ in Hz): δ 134.2, 131.5 (proximal and distal carbons of C_5Me_4 , s), 101.0 (bridgehead carbon, s), 56.7 ($NCMe_3$, s), 33.0 ($NCMe_3$, q, 125), 14.7, 12.0 (C_5Me_4 , q, 128), 6.01 ($SiMe_2$, q, 120).

Preparation of Diphenyl Derivatives

(a) Synthesis of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$

A 1.50 g sample (4.8 mmol) of $[(C_5H_4)SiMe_2(N-t-Bu)]TiCl_2$ was placed in a two neck round bottom flask with one neck capped with a suba-seal septum extension and the second neck attached to a filter frit assembly. Diethyl ether (*ca.* 30 mL) was added by vacuum distillation. The reaction mixture was then cooled in a liquid $N_2/2$ -propanol bath. While stirring under a N_2 flush, 3.20 mL (3.0M in Et_2O) $PhMgBr$ was added dropwise via syringe over a 45 minute period. The solution was then allowed to warm to room temperature and stirred overnight. During the course of the reaction, the original orange color of the solution became deep red. The solvent was removed under reduced pressure and product was extracted from the remaining residue with an equal amount of pentane and filtered. Removal of the pentane left 1.08 g (56.6% yield) of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$ as a dark red solid. 1H NMR (C_6D_6 , $^3J_{HH}$ in Hz): δ 8.14, 7.20, 7.09 (C_6H_5 , m), 6.56, 5.27 (C_5H_4 , t, 2.1), 0.90 ($NCMe_3$, s), 0.61 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR (C_6D_6 , $^1J_{CH}$ in Hz): δ 188.4 (ipso-carbon of C_6H_5 , s), 133.7, 128.7, 126.7 (C_6H_5 , d, 169), 118.5, 118.0 (proximal

and distal carbons of C₅H₄, d, 169), 110.5 (bridgehead carbon, s), 60.5 (NCMe₃, s), 33.8 (NCMe₃, q, 124), 1.51 (SiMe₂, q, 118).

(b) Synthesis of [(C₅H₄)SiMe₂(N-t-Bu)]Zr(C₆H₅)₂

A 0.503 g sample (1.41 mmol) of {[(C₅H₄)SiMe₂(N-t-Bu)]ZrCl(μ-Cl)}₂ was placed in a two neck round bottom flask with a cylindrical glass extension capped with a suba-seal septum attached to one neck. Diethyl ether (*ca.* 30 mL) was added by vacuum distillation. The reaction mixture was then cooled in a liquid N₂/2-propanol bath. While stirring under a N₂ flush, 1.57 mL of a 1.8M THF solution of PhMgCl was added dropwise over a 45 minute period. The solution was then allowed to stir for one hour and the temperature was slowly allowed to rise to 0°C. The solvent was removed under reduced pressure and product was extracted from the remaining off-white residue with an equal amount of pentane. Removal of pentane left 0.559 (90.0% yield) of [(C₅H₄)SiMe₂(N-t-Bu)]Zr(C₆H₅)₂ as a light yellow residue. Note: The color of the isolated product slowly darkens, an indication that this compound is thermodynamically unstable at ambient temperature. ¹H NMR (C₆D₆, ³J_{HH} in Hz): δ 7.74, 7.27, 7.21 (C₆H₅, m), 6.34 (C₅H₄, s), 1.24 (NCMe₃, s), 0.43 (SiMe₂). ¹H NMR (CDCl₃, ³J_{HH} in Hz): δ 7.40, 7.37, 7.04 (C₆H₅, m), 6.43, 6.25 (C₅H₄, t, 2.3), 1.15 (NCMe₃, s), 0.36 (SiMe₂, s). ¹³C{¹H} NMR (CDCl₃): δ 183.7 (ipso-carbon of C₆H₅), 134.6, 127.7, 126.8 (C₆H₅), 121.2, 118.0 (proximal and distal carbons of C₅H₄), 105.0 (bridgehead carbon), 56.7 (NCMe₃), 33.6 (NCMe₃), 1.43 (SiMe₂).

(c) Synthesis of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$

A 1.00 g sample (2.4 mmol) of $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrCl_2$ was placed in a two neck round bottom flask where one neck was capped with a suba-seal septum adapter. Diethyl ether (*ca.* 30 mL) was added by vacuum distillation. The reaction mixture was then cooled in a liquid $N_2/2$ -propanol bath. While stirring under a N_2 flush, 2.7 mL of a 1.8 M cyclohexane-ether solution of PhLi was added dropwise over a 45 minute period. The reaction mixture was then allowed to stir for one hour and the temperature was slowly raised to 0°C. The solvent was removed under reduced pressure and the product was extracted with an equal amount of pentane. Removal of pentane left 0.903 g (74.7% yield) of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ as a light tan solid. 1H NMR ($CDCl_3$, $^3J_{HH}$ in Hz): δ 7.48, 7.09, 7.06 (C_6H_5 , m), 1.93, 1.61 (C_5Me_4 , s), 1.29 ($NCMe_3$, s), 0.52 ($SiMe_2$, s). Gated nondecoupled ^{13}C NMR ($CDCl_3$, $^1J_{CH}$ in Hz): δ 188.1 (ipso-carbon of C_6H_5 , s), 135.1 (C_6H_5 , d, 162), 131.7, 127.4 (proximal and distal carbons of C_5Me_4 , s), 127.2, 126.5 (C_6H_5 , d, 157), 97.2 (bridgehead carbon, s), 56.8 ($NCMe_3$, s), 15.0, 11.9 (C_5Me_4 , q, 121, 126), 33.5 ($NCMe_3$, q, 124), 6.44 ($SiMe_2$, q, 121).

Diphenylacetylene Coupling Reactions

(a) Synthesis of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$

A 0.492 g sample (1.24 mmol) of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$ was combined with 0.222 g (1.24 mmol) of diphenylacetylene in a 100 mL round bottom flask, which was attached to a filter frit assembly. Cyclohexane (*ca.* 20mL) was added via vacuum transfer and the reaction mixture was stirred at 80°C overnight. Solvent was removed under reduced pressure and the dark

red product residue was washed with hexamethyldisiloxane. Recrystallization by slow removal of pentane from a concentrated solution yielded reddish-orange crystals of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$ suitable for an X-ray crystallographic analysis. Anal. Calcd. for $C_{31}H_{33}NSiTi$ (495.58): C, 75.12; H, 6.71; N, 2.82. Found: C, 75.69; H, 6.38; N, 2.72. The NMR data are given in Table 1.

(b) Synthesis of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[(C_6H_4)C(Ph)=C(Ph)]$

A 1.00 g sample (2.02 mmol) of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ was combined with 0.360 g (2.02 mmol) of diphenylacetylene in a 100 mL round bottom flask. Cyclohexane (*ca.* 50 mL) was added via vacuum transfer and the reaction mixture was stirred at 60°C for two days. Solvent was removed under reduced pressure. Repeated washings with hexamethyldisiloxane yielded $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[(C_6H_4)C(Ph)=C(Ph)]$ as a dry off-white solid. Anal. Calcd. for $C_{35}H_{41}NSiZr$ (595.02): C, 70.64; H, 6.94; N, 2.35. Found: C, 65.14; H, 6.46; N, 1.11. The NMR data are summarized in Table 2.

Table 1. ^1H and ^{13}C NMR data for $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Ti}[(\text{C}_6\text{H}_4)\text{C}(\text{Ph})=\text{C}(\text{Ph})]$.Solvent: CDCl_3

Peak Assignment	^1H NMR	^{13}C NMR
SiMe_2	0.49; 0.59	0.75; 1.01
NCMe_3	1.58	34.0
C_5H_4	5.55; 6.20	126.0; 126.4
	7.03; 7.47	121.8; 122.05
NCMe_3		60.1
C_b^a		107.9
C_6H_4	6.50	126.5
	6.83	124.7
	6.96	128.2
	7.00	127.4
C_6H_5	6.70	131.05
	6.75	125.7
	6.83	123.7
	7.05	129.8
	7.13	126.2
	7.18	127.8
	<i>ipso-C</i>	138.9
	<i>ipso-C</i>	144.4
Ti-C=C		147.9; 145.8
Ti-C		206.1; 193.7

^a C_b corresponds to the bridgehead C attached to Si.

Table 2. ^1H and ^{13}C NMR data for $[(\text{C}_5\text{Me}_4)\text{SiMe}_2(\text{N-t-Bu})\text{Zr}[(\text{C}_6\text{H}_4)\text{C}(\text{Ph})=\text{C}(\text{Ph})]]$.Solvent: CDCl_3

Peak Assignment	^1H NMR	^{13}C NMR
SiMe_2	0.53; 0.61	6.36; 6.51
NCMe_3	1.54	33.7
C_5Me_4	1.52; 1.95	13.3; 12.2
	1.97; 2.22	11.45; 13.9
NCMe_3		56.2
C_b^a		97.4
C_5Me_4		127.9; 128.6
		132.7; 132.8
C_6H_4	6.55	126.9
	6.79	123.2
	6.96	127.2
	7.01	128.1
C_6H_5	6.86	127.8
	6.94	124.8
	6.98	130.1
	7.12	125.7
	7.18	127.6
	7.22	133.1
	<i>ipso-C</i>	140.9
	<i>ipso-C</i>	144.7
Zr-C=C		150.5; 146.3
Zr-C		197.2; 186.7

^a C_b corresponds to the bridgehead C attached to Si.

X-Ray Structural Analysis of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_4C(Ph)=C(Ph))$.

A reddish orange crystal of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_4C(Ph)=C(Ph))$ was sealed in a glass capillary tube under a nitrogen atmosphere and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The reflections that were used for the unit cell determination were located and indexed by the automatic peak search routine provided with XSCANS.³⁶ An I-centered monoclinic cell was originally used for purposes of data collection and then converted to the conventional C-centered cell prior to performing the structural analysis. The lattice parameters and orientation matrix for the I-centered cell were calculated from a non-linear least-squares fit of the orientation angles of 30 reflections at 22 °C. The systematic absences for {h k l} data with $h + k + l = 2n + 1$ absent and {h 0 l} data with $h = 2n + 1$ data absent are consistent with the space groups Ia and I2/a, which correspond to nonstandard settings of Cc (C_5^4 , No. 9) and C2/c (C_{2h}^6 , No. 15), respectively. Of these two choices the results of the structural analysis confirmed that the centrosymmetric case to be the correct one. The lattice parameters and other pertinent crystallographic information are summarized in Table 3.

Intensity data were measured with graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and variable ω scans (2-10°/min). Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections, which were measured after every 100 reflections, showed no indication of crystal decomposition or sample movement. The raw data were corrected for Lorentz-polarization effects.

Initial coordinates for the non-hydrogen atoms were determined by a combination of direct methods and difference Fourier calculations performed with the algorithms provided in SHELXTL-IRIS operating on a Silicon Graphics Iris Indigo workstation. The hydrogen atom positions were idealized with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The positions of the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinement with SHELXL-93,³⁷ based upon the minimization of $\sum w_i |F_o^2 - F_c^2|^2$ with weighting given by the expression $w_i^{-1} = [\sigma^2(F_o^2) + (0.0586 P)^2]$ where $P = (\text{Max}(F_o^2, 0) + 2 F_c^2)/3$, converged to give the values of the final discrepancy indices³⁸ provided in Table 3.

Table 3. Crystallographic Data for the Structural Analysis of [(C₅H₄)SiMe₂(N-t-Bu)]Ti(C₆H₄C(Ph)=C(Ph)).

A. Crystal Data

emp. formula	C ₃₁ H ₃₃ NSiTi
color	red orange
crystal dimensions, mm	0.15 x 0.34 x 0.36
crystal system	monoclinic
space group	C2/c
a, Å	30.993(3)
b, Å	11.418(2)
c, Å	16.616(2)
β, deg	109.55(1)
Volume, Å ³	5541.1(11)
Z	8
formula weight, amu	495.57
calc density, g/cm ³	1.188
μ, cm ⁻¹	3.71
F(0 0 0)	2096
temperature, °C	22 ± 1

B. Data Collection and Structural Analyses

scan type	ω, variable
scan rate, deg/min	2.0 - 10.0
2θ range, deg	3.0 - 40.0
2θ range, centered refls	10 - 25
reflections sampled	h (-18 ≤ h ≤ 33) k (-12 ≤ k ≤ 1) l (-17 ≤ l ≤ 17)
no. of refl. collected	4287
no. of unique data	3558 (R _{int} = 0.0473)
no. of data, I > 2σ(I)	1769
R indices, I > 2σ(I)	R1 = 0.0636 wR2 = 0.1206
R indices, all data	R1 = 0.1627 wR2 = 0.1896
σ ₁ , GOF	1.020
no. of variables	312
max. diff. peak and hole	0.208, -0.221

Table 4. Interatomic Distances (Å) and Bond Angles for [(C₅H₄)SiMe₂(N-t-Bu)]Ti(C₆H₄C(Ph)=C(Ph)).^a

A. Interatomic Distances

Ti-N	1.915(5)	Ti-Cp(c)	2.025
Ti-C(12)	2.081(7)	Ti-C(15)	2.103(6)
Ti-C(1)	2.299(6)	Ti-C(2)	2.332(2)
Ti-C(3)	2.379(7)	Ti-C(4)	2.410(7)
Ti-C(5)	2.332(7)	N-C(8)	1.489(7)
Si-N	1.744(5)	Si-C(1)	1.855(8)
Si-C(6)	1.850(8)	Si-C(7)	1.845(7)
C(1)-C(2)	1.416(9)	C(2)-C(3)	1.380(9)
C(3)-C(4)	1.383(10)	C(4)-C(5)	1.391(10)
C(5)-C(1)	1.411(9)	C(8)-C(9)	1.516(8)
C(8)-C(10)	1.530(9)	C(8)-C(11)	1.548(8)
C(12)-C(13)	1.404(8)	C(13)-C(14)	1.511(8)
C(14)-C(15)	1.355(8)	C(12)-C(16)	1.390(8)
C(13)-C(19)	1.381(8)	C(14)-C(20)	1.511(8)
C(15)-C(26)	1.469(8)	C(16)-C(17)	1.381(8)
C(17)-C(18)	1.363(8)	C(18)-C(19)	1.386(9)

B. Bond Angles

Cp(c)-Ti-N	108.4	Cp(c)-Ti-C(12)	115.3
Cp(c)-Ti-C(15)	118.2	N-Ti-C(12)	110.8(2)
N-Ti-C(15)	117.5(2)	C(12)-Ti-C(15)	85.1(3)
C(12)-Ti-Si	129.8(2)	C(15)-Ti-Si	137.8(2)
N-Si-C(1)	93.4(3)	N-Si-C(7)	116.0(3)
N-Si-C(6)	113.4(3)	C(1)-Si-C(6)	110.1(4)
C(1)-N-C(7)	111.8(4)	C(6)-Si-C(7)	111.0(4)
Si-N-Ti	103.4(2)	C(8)-N-Si	126.4(4)
C(8)-N-Ti	129.7(4)	C(2)-C(1)-C(5)	104.2(6)
C(2)-C(1)-Si	121.8(6)	C(5)-C(1)-Si	121.5(6)
C(1)-C(2)-C(3)	109.4(7)	C(2)-C(3)-C(4)	109.2(8)
C(3)-C(4)-C(5)	106.5(8)	C(4)-C(5)-C(1)	110.7(8)

N-C(8)-C(9)	111.3(6)	N-C(8)-C(10)	110.0(6)
N-C(8)-C(11)	108.9(5)	C(9)-C(8)-C(10)	109.9(6)
C(9)-C(8)-C(11)	108.3(6)	C(10)-C(8)-C(11)	108.4(6)
C(13)-C(12)-Ti	108.4(5)	C(16)-C(12)-Ti	133.2(5)
C(13)-C(12)-C(16)	118.2(6)	C(12)-C(13)-C(14)	118.1(6)
C(12)-C(13)-C(19)	120.3(6)	C(14)-C(13)-C(19)	121.7(6)
C(13)-C(14)-C(15)	119.0(6)	C(13)-C(14)-C(20)	116.2(5)
C(15)-C(14)-C(20)	124.9(6)	C(14)-C(15)-C(26)	124.9(6)
C(14)-C(15)-Ti	109.0(5)	C(26)-C(15)-Ti	125.9(5)
C(12)-C(16)-C(17)	121.4(7)	C(16)-C(17)-C(18)	119.4(7)
C(17)-C(18)-C(19)	121.1(7)	C(13)-C(19)-C(18)	119.7(6)

^a Cp(c) corresponds to the centroid of the five-membered cyclopentadienyl ring.

Results and Discussion

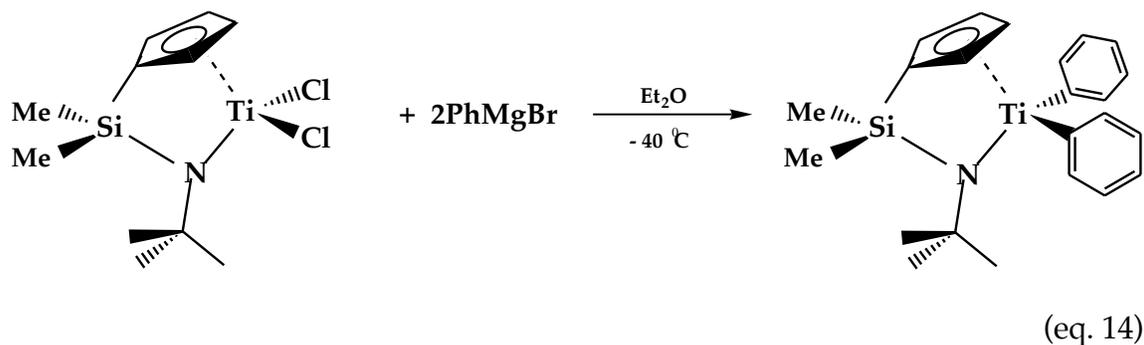
Preparation of $[(C_5R_4)SiMe_2(N-t-Bu)]M(C_6H_5)_2$ where $R=H, Me$; $M=Ti, Zr$.

The series of *ansa*-mono- and *ansa*-tetramethylcyclopentadienyl metal diphenyl complexes were prepared by the stoichiometric metathetical reaction of the corresponding metal dichloride precursor with two equiv. of an appropriate phenylating reagent. The phenylating reagents that were considered included phenyllithium, phenylmagnesiumbromide, and phenylmagnesiumchloride. The utilization of a specific phenyl reagent is not general for the preparation of these diphenyl complexes, but instead is dependent on the choice of the dichloride precursor.

(a) Preparation of the *ansa*-monocyclopentadienyl Ti(IV) diphenyl complex,



The stoichiometric reaction of $[(C_5H_4)SiMe_2(N-t-Bu)]TiCl_2$ with two equivalents of $PhMgBr$ was carried out in ether at $-40^\circ C$, eq. 14. As the reaction temperature increased to room temperature, the color of the solution turned from orange to deep red. The product, $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$, was extracted with pentane and in 56% yield as a semi-crystalline reddish-orange solid.



The identity of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$ was verified by solution 1H and ^{13}C NMR measurements in C_6D_6 . Both sets of NMR data are consistent with the presence of mirror symmetry in solution. The 1H NMR spectrum contains multiplets at δ 8.14 and 7.09 for the *ortho*- and *meta*-protons and a signal at δ 7.20 for the *para*-protons of the phenyl substituents. The 1H NMR signal at δ 7.20 is obscured somewhat by the proton resonance of residual C_6D_5H . Two pseudo triplets for the distal and proximal protons of the cyclopentadienyl group are centered at δ 6.56 and δ 5.27. The singlet at δ 1.58 represents the nine methyl protons of the t-butyl amido substituent. A singlet for the six methyl protons of the $SiMe_2$ bridge is found at δ 0.61 .

The corresponding $^{13}C\{^1H\}$ NMR spectrum exhibits the expected number of ten carbon resonances. The values for the $^1J_{CH}$ coupling constants were obtained from the measurements of the gated non-decoupled ^{13}C NMR spectrum. The ^{13}C NMR data for $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$ are summarized in Table 5. The two methyl carbons of the $SiMe_2$ bridge appear as a quartet at δ 1.51 ($^1J_{CH}= 118$ Hz); the three methyl carbons of the tert-butyl substituent and the quaternary carbon of the amido functionality exhibit a quartet at δ 33.8 ($^1J_{CH}= 124$ Hz) and a singlet at δ 60.5, respectively. The cyclopentadienyl group displays a singlet at δ 110.5 for the bridgehead carbon and a pair of doublet of multiplets at δ 118.5 ($^1J_{CH}= 169$ Hz) and δ 118.0 ($^1J_{CH}= 169$ Hz) for the proximal and distal cyclopentadienyl ring carbons. The phenyl carbons appear as doublets at δ 126.7 and 133.7 with a $^1J_{CH}= 169$ Hz for the *meta*-, and *ortho*-carbons and a doublet at δ 128.7 with $^1J_{CH}= 169$ Hz for the *para*-carbons of the phenyl substituents; the singlet at δ 188.4 represents the carbon atoms directly attached to the metal.

	δ in ppm	$(^1J_{\text{CH}})$
C10	s 188.4	
C9, C8 C7	d 133.7, 128.7, 126.7	169 Hz
C6	d 118.5	169 Hz
C5	d 118.0	169 Hz
C4	s 110.5	
C3	s 60.5	
C2	q 33.8	124 Hz
C1	q 1.51	118 Hz

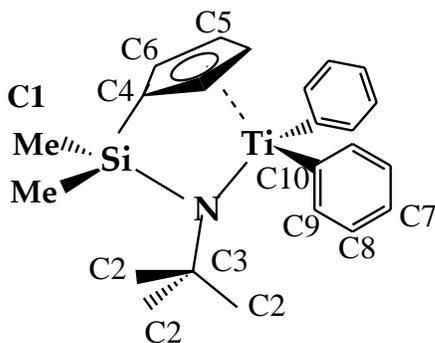
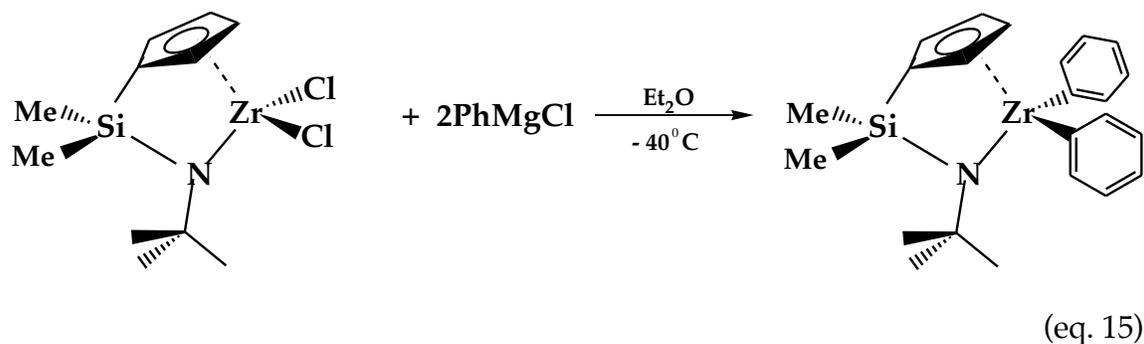


Table 5. ^{13}C NMR data for $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Ti}(\text{C}_6\text{H}_5)_2$.

**(b) Preparation of the ansa-monocyclopentadienyl Zr(IV) diphenyl complex,
 $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Zr}(\text{C}_6\text{H}_5)_2$**

The metathetical reaction of $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{ZrCl}_2$ with two equivalents of PhMgCl similarly proceeded with the formation of the corresponding zirconium diphenyl complex, $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Zr}(\text{C}_6\text{H}_5)_2$, as shown in eq. 15. The reaction was carried out at -40°C in ether.

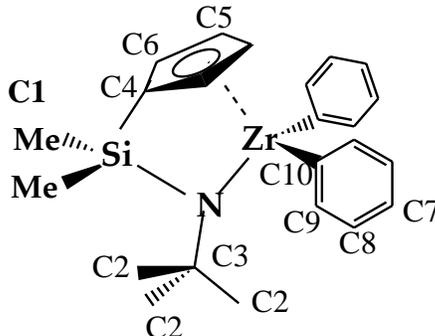


This compound was also isolated by extraction with pentane, affording initially a light yellow residue in 90% yield. However, within a few hours this compound darkened upon standing at ambient temperature. This color change was accompanied by deterioration of the NMR spectral features for $[(C_5H_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$.

The identity of $[(C_5H_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ was verified by solution 1H and ^{13}C NMR measurements in C_6D_6 and $CDCl_3$. The NMR data are consistent with the presence of mirror-symmetry in solution and show that the chemical shifts of the cyclopentadienyl ring protons are highly solvent dependent. In C_6D_6 , the *ortho*- and *meta*-protons of the phenyl ligands appear at δ 7.74 and 7.21 with the *para*-protons appearing at δ 7.27. The distal and proximal protons of the cyclopentadienyl ring exhibit only an apparent singlet at δ 6.34. The singlet at δ 1.24 is assigned to the t-butyl nine methyl protons of the amido functionality and the upfield singlet at δ 0.61 corresponds to the six methyl protons of the $SiMe_2$ bridge. To resolve the two resonances expected for the pairs of the distal and proximal cyclopentadienyl ring protons, the 1H NMR spectrum was also measured in $CDCl_3$. This spectrum contains three multiplets at δ 7.40, 7.37, and 7.04 corresponding to the phenyl ring protons, two pseudo triplets at δ 6.43 and δ 6.25 for the distal and proximal protons of the cyclopentadienyl ring, a singlet at δ 1.15 representing the nine methyl protons of the t-butyl amido substituent and a singlet at δ 0.36 for the six methyl protons of the $SiMe_2$ bridge.

The corresponding $^{13}C\{^1H\}$ NMR spectrum of $[(C_5H_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$, in $CDCl_3$, exhibits the expected ten carbon resonances. The ^{13}C NMR data for $[(C_5H_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ are summarized in Table 6. The two methyl carbons of the $SiMe_2$ bridge appear at δ 1.43, the three methyl carbons and the quaternary carbon of the t-butyl substituent appear at δ 33.6

and δ 56.7, respectively. The cyclopentadienyl ring carbons exhibit three resonances, with the signal at δ 105.0 representing the bridgehead carbon and the downfield resonances at δ 121.2 and δ 118.0 corresponding to the proximal and distal carbons of the cyclopentadienyl ring. Two resonances appearing at δ 134.6 and 126.8 represent the *ortho*- and *meta*-carbons of the phenyl ring with a signal at δ 127.7 assigned to the *para*-carbons. The downfield signal at δ 183.7 is assigned to the carbon atoms of the phenyl rings directly bonded to zirconium.

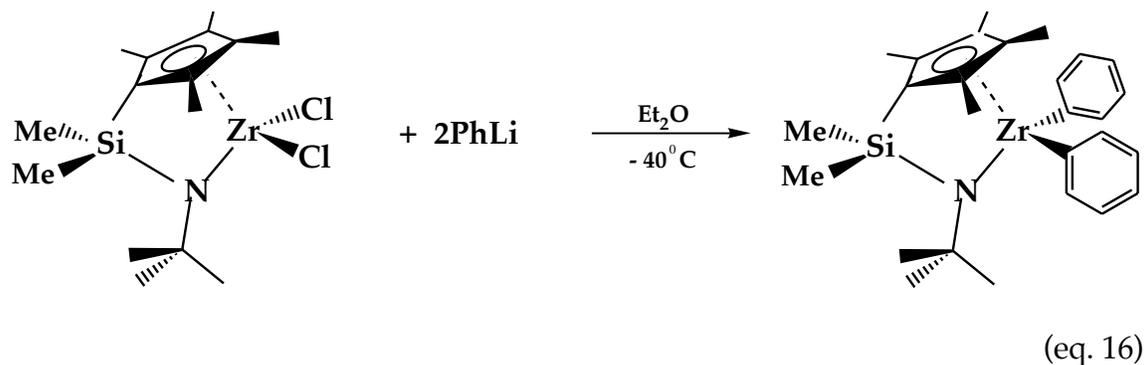


	δ in ppm
C10	183.7
C9, C8 C7	134.6, 127.7, 126.8
C6	121.2
C5	118.0
C4	105.0
C3	56.7
C2	33.6
C1	1.43

Table 6. ^{13}C NMR data for $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Zr}(\text{C}_6\text{H}_5)_2$.

(c) Preparation of the ansa-tetramethylcyclopentadienyl Zr(IV) diphenyl complex, $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$

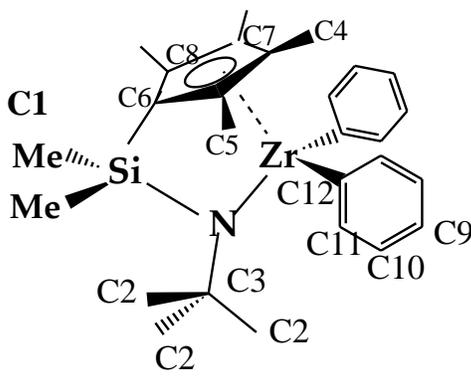
Treatment of $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrCl_2$ with two equivalents of PhLi, when carried out in ether at $-40^\circ C$, proceeded cleanly with the formation of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ (eq. 16). This diphenyl compound was obtained as a light tan solid in 74.7% yield and is highly soluble in pentane.



The identity of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ was confirmed by solution 1H and ^{13}C NMR measurements in $CDCl_3$. The NMR data are consistent with the presence of mirror symmetry. The 1H NMR spectrum contains multiplets at δ 7.48 and 7.06 for the *ortho*- and *meta*- protons and a signal at δ 7.09 for the *para*-protons of the phenyl ligands. The spectrum further contains two singlets at δ 1.93 and δ 1.61 for the distal and proximal methyl protons of the C_5Me_4 ring, a singlet at δ 1.29 for the nine methyl protons of the appended *t*-butyl amido functionality, and an upfield singlet at δ 0.52 for the six methyl protons of the $SiMe_2$ bridge.

The $^{13}C\{^1H\}$ NMR spectrum exhibits the expected number of twelve carbon resonances. The values for the $^1J_{CH}$ coupling constants were obtained from the measurement of the gated non-decoupled ^{13}C NMR spectrum. The ^{13}C NMR data for $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ are summarized in Table 7. The two methyl carbons of the $SiMe_2$ linkage appear as a binomial quartet

at δ 6.44 ($^1J_{\text{CH}} = 121$ Hz), the three methyl carbons of the tert-butyl substituent and the quaternary carbon of the amido functionality exhibit a quartet at δ 33.5 ($^1J_{\text{CH}} = 124$ Hz) and a singlet at δ 56.8, respectively. The methyl carbons of the tetramethylcyclopentadienyl ring display a pair of quartets at δ 15.0 ($^1J_{\text{CH}} = 121$ Hz) and δ 11.9 ($^1J_{\text{CH}} = 126$ Hz) for the proximal and distal methyl carbons. The three carbon resonances of the cyclopentadienyl ring appear as a singlet at δ



	δ in ppm	$(^1J_{\text{CH}})$
C12	s 188.1	
C11, C10	d 135.1, 127.2, 126.5	157 Hz
C9		
C8	s 131.7	
C7	s 127.4	
C6	s 97.2	
C5	q 11.9	121 Hz
C4	q 15.0	126 Hz
C3	s 56.8	
C2	q 33.5	124 Hz
C1	q 6.44	121 Hz

Table 7. ^{13}C NMR data for $[(\text{C}_5\text{Me}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Zr}(\text{C}_6\text{H}_5)_2$.

97.2 for the bridgehead carbon and a pair of singlets at δ 131.7 and δ 127.4 representing the proximal and distal ring carbons. The phenyl carbons appear as doublets at δ 126.5 and δ 135.1 with a $^1J_{\text{CH}} = 157$ Hz for the *ortho*- and *meta*-carbons and a doublet at δ 127.2 ($^1J_{\text{CH}} = 162$ Hz) for the *para*-carbons. The singlet at δ 188.1 represents the carbon atoms directly bonded to zirconium.

Diphenylacetylene Coupling Reactions

The thermally-induced reactions of diphenylacetylene with a diphenyl precursor were performed in an effort to trap the benzyne intermediate and to isolate the resultant five membered metallacyclic product. Erker and co-workers¹² reported that aromatic solvents do participate in the thermolysis of diarylmetallocenes. In order to prevent the ring exchange between the σ -bonded phenyl ligands bound to the metal and an aromatic solvent, these reactions were carried out in cyclohexane.

(a) Synthesis of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$

The coupling reaction involving $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$ and diphenylacetylene was heated in cyclohexane at 80°C (Figure 5). The reaction proceeded smoothly with the formation of one primary product. The resulting deep red product residue was washed with minimal amounts of hexamethyldisiloxane. Reddish-orange crystals of the product, $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$ were isolated after recrystallization from a concentrated pentane solution. These crystals were found to be suitable for an X-ray structural analysis (*vide infra*).

The reaction conditions differ somewhat from those used for the coupling reaction of diphenylacetylene and $(C_5H_5)_2Ti(C_6H_5)_2$.⁹ Here, cyclohexane rather than benzene was used as the solvent with the reaction time being extended to 24h to ensure completion.

The coupling reaction is believed to proceed initially with intramolecular elimination of benzene to produce a benzyne intermediate.

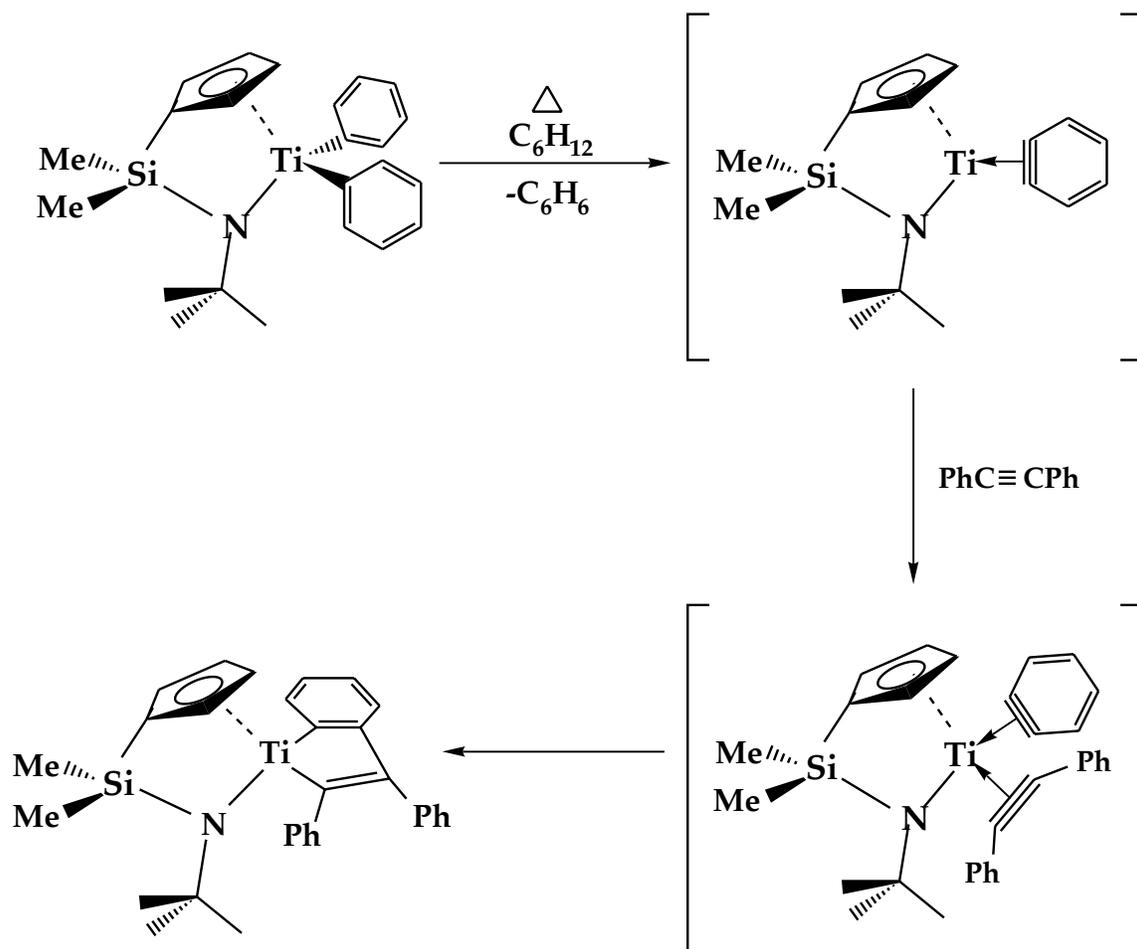


Figure 5. Coupling reaction of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$ with diphenylacetylene.

This electrophilic species is presumably stabilized by complexation of diphenylacetylene. Following complexation, intramolecular C-C bond

coupling proceeds with the formation of the titanacyclopentadiene product (Figure 5).

The identity of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$ was verified by solution 1H and ^{13}C NMR measurements along with 2D HETCOR and COSY NMR measurements in $CDCl_3$. The NMR data indicate that the molecule lacks mirror symmetry in solution. Due to the presence of many overlapping resonances in the aromatic regions of the ^{13}C and 1H NMR spectra, 2D NMR techniques were employed in order to identify and assign the individual resonances. The 1H NMR spectrum contains peaks at δ 7.18, 7.13, 7.05, 6.83, 6.75, and 6.70 for the six inequivalent protons on the two independent phenyl substituents of the titanacyclopentadiene ring. The four benzyne proton resonances are found as doublets at δ 7.00, 6.96, 6.83, and 6.50, with the four chemically inequivalent protons of the cyclopentadienyl group appearing as pseudo triplets at δ 7.47, 7.03, 6.20, and 5.55. There is a singlet at δ 1.58 representing the nine methyl protons of the *t*-butyl group and two singlets at δ 0.59 and δ 0.49 for the two inequivalent methyl groups of the $SiMe_2$ bridge.

The 1H NMR resonances for the cyclopentadienyl and benzyne functional groups were subsequently verified by the 2D COSY NMR spectrum, which contains an off-diagonal peak for each pair of coupled protons (Figure 6). The benzyne proton resonance at δ 6.50 has three off-diagonal peaks at δ 6.83, 6.96, and 7.00 due to coupling with the three other benzyne proton signals. The remaining three proton chemical shifts for the benzyne functionality all exhibit three off-diagonal peaks consistent with the assignment of these resonances to the benzyne functionality.

In the case of the cyclopentadienyl group, the four distal and proximal protons are diastereotopic and therefore exhibit four distinct resonances. The

peak at δ 7.47 is coupled to two other protons at δ 7.03 and δ 6.20. The resonance at δ 7.03 is coupled to the protons at δ 7.47 and δ 5.55. The peak centered at δ 6.20 is coupled to proton resonances at δ 7.47 and δ 5.55. The peak at δ 5.55 indicates coupling to the two signals centered at δ 7.03 and δ 6.20.

The corresponding $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits the expected number of twenty five carbon resonances. Due to the large number of overlapping resonances, a 2D HETCOR NMR spectrum was recorded to assist in the assignment of the carbon resonances (Figure 7). The 2D HETCOR NMR spectrum made it possible to assign the carbon signals associated with specific fragments within the molecule by analyzing the ^{13}C and ^1H chemical shifts associated with the observed peaks. Each peak in the HETCOR spectrum corresponds to a carbon bearing one or more hydrogen atoms with its position correlating the respective chemical shifts for the corresponding carbon and proton signals. The quaternary carbons can be distinguished from carbon atoms bearing protons by the fact that these carbons do not exhibit a peak in the HETCOR spectrum. The two methyl carbons of the SiMe_2 bridge appear at δ 0.75 and δ 1.01. The three methyl carbons and the quaternary carbon of the amido functionality appear at δ 34.0 and δ 60.1, respectively. The cyclopentadienyl group exhibits five resonances with the signal at δ 107.9 representing the bridgehead carbon and the four resonances at δ 121.8, 122.05, 126.0, and 126.4 corresponding to the four remaining carbon atoms of the cyclopentadienyl ring. There are six carbon resonances for the benzyne functionality, where the signals at δ 124.7, 126.5, 127.4, and 128.2 correspond to the four carbons bearing hydrogens and the two peaks at δ 145.8 and δ 193.7 represent two quaternary carbons within the five-membered

Figure 6. 2D COSY NMR spectrum for
 $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$.

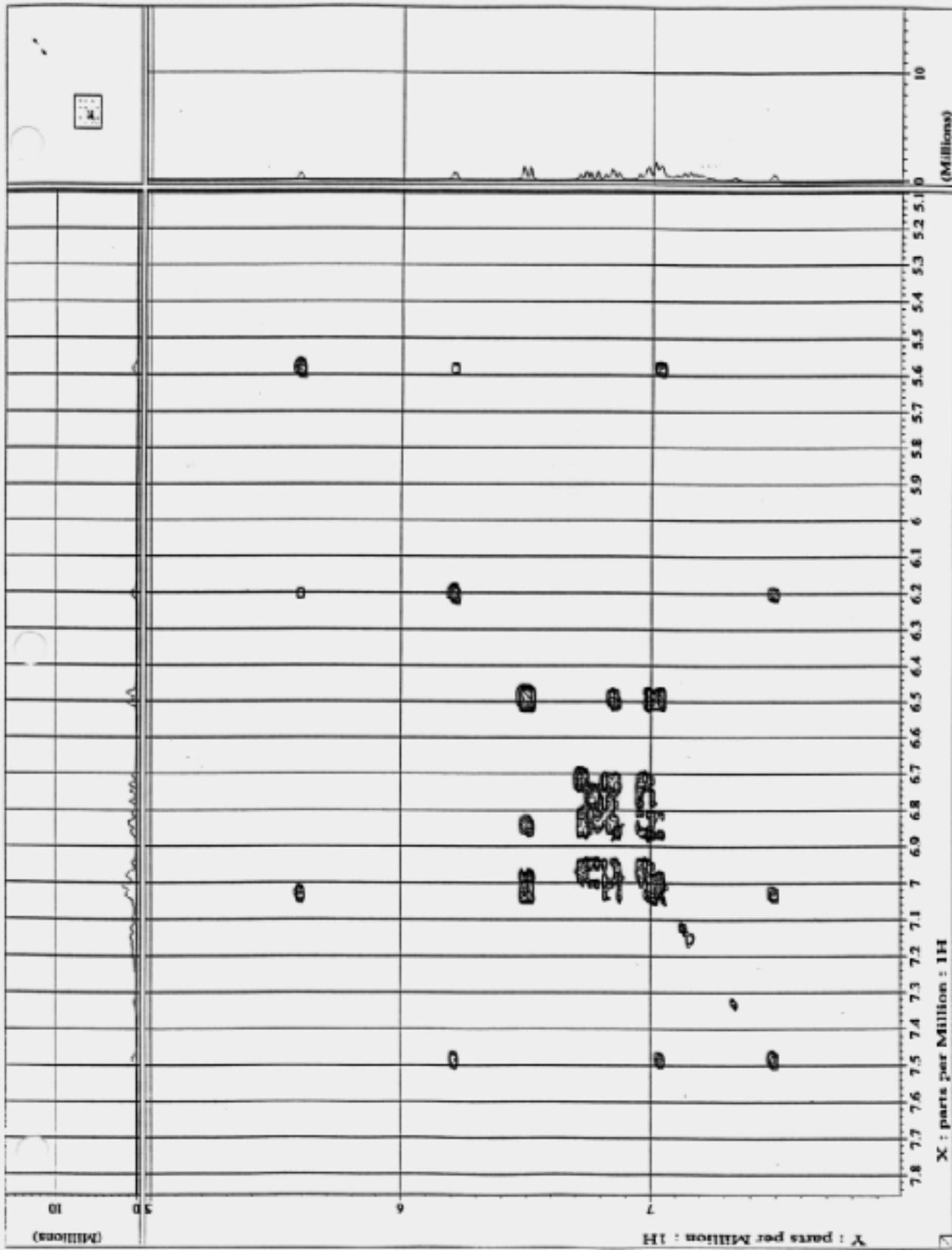
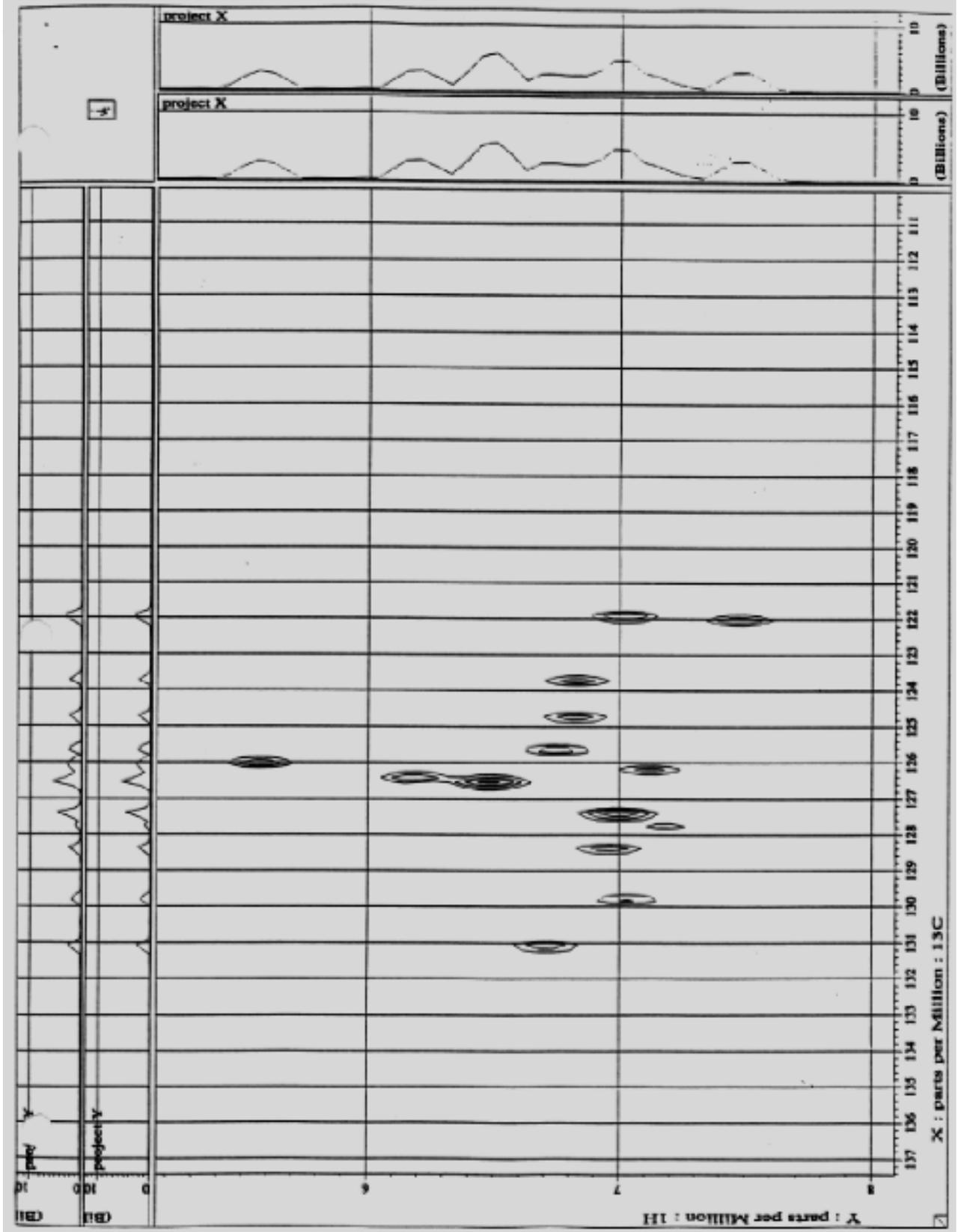


Figure 7. 2D HETCOR NMR spectrum measured for
 $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$.



titanacyclopentadiene ring. The two phenyl substituents of the metallacycle exhibit the expected eight carbon resonances, with the signals at δ 123.7, 125.7, 126.2, 127.8, 129.8, and 131.05 representing the *ortho*-, *meta*-, and *para*-carbons of the phenyl rings and the two resonances at δ 138.9 and δ 144.4 assigned to the two ipso-quaternary carbons. The two resonances at δ 147.9 and δ 206.1 correspond to the two remaining carbons of the five membered titanacyclic ring.

(b) Synthesis of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[(C_6H_4)C(Ph)=C(Ph)]$

The coupling reaction between $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ and diphenylacetylene was carried out in cyclohexane, (Figure 8). The reaction mixture was heated to 60°C for two days resulting in the formation of a crude product mixture from which the desired product was isolated after numerous washings with hexamethyldisiloxane. The product was isolated as a dry off-white solid. This coupling reaction presumably proceeds in a similar manner to that proposed for the formation of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$ (Figure 8).

The identity of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[(C_6H_4)C(Ph)=C(Ph)]$ was verified by solution 1H and ^{13}C NMR measurements along with 2D HETCOR and COSY NMR measurements in $CDCl_3$. As expected, the solution NMR data indicate that the molecule lacks mirror symmetry. With the presence of many overlapping resonances in the aromatic regions of both 1H and ^{13}C NMR spectra, 2D NMR techniques were employed to aid in the assignment of individual resonances. The 1H NMR spectrum contains peaks at δ 7.22, 7.18, 7.12, 6.98, 6.94, and 6.86 for the six inequivalent protons of the two independent phenyl substituents of the zirconacyclopentadiene ring. The

chemical shifts of the four proton resonances of the benzyne functionality at δ 7.01, 6.96, 6.79, and 6.55 are similar to those for the benzyne proton resonances in $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$. This spectrum further contains four singlets at δ 2.22, 1.97, 1.95, and 1.52 for the four sets of methyl protons on the tetramethylcyclopentadienyl ring and a singlet at δ 1.54 representing the nine methyl protons of the appended t-butyl amido functionality. There are two singlets at δ 0.61 and δ 0.53 for the two inequivalent methyl groups of the $SiMe_2$ bridge.

The 1H NMR resonances for the benzyne functionality were subsequently verified by the 2D COSY NMR spectrum. Each off-diagonal peak indicates coupling between pairs of protons (Figure 9). The benzyne proton resonance at δ 6.55 has three off-diagonal peaks at δ 6.79, 6.96, and 7.01 due to coupling with the three other benzyne proton signals. These three other protons of the benzyne functionality also exhibit three off-diagonal peaks consistent with their assignment to the benzyne functionality.

The corresponding $^{13}C\{^1H\}$ NMR spectrum exhibits the expected number of twenty nine carbon resonances. With the large number of overlapping resonances, a 2D HETCOR NMR measurement was taken to aid in the assignment of the carbon resonances (Figure 10). The 2D HETCOR NMR correlates chemical shifts between ^{13}C and 1H nuclei that are directly bonded to one another. Quaternary carbon resonances can be assigned from the fact that no peaks are observed for carbons lacking protons. The two methyl carbons of the $SiMe_2$ bridge appear at δ 6.36 and δ 6.51. The three methyl carbons and the quaternary carbon of the t-butyl amido functionality appear at δ 33.7 and δ 56.2, respectively. The methyl carbons of the tetramethylcyclopentadienyl ring display four resonances at δ 13.9, 13.3, 12.2,

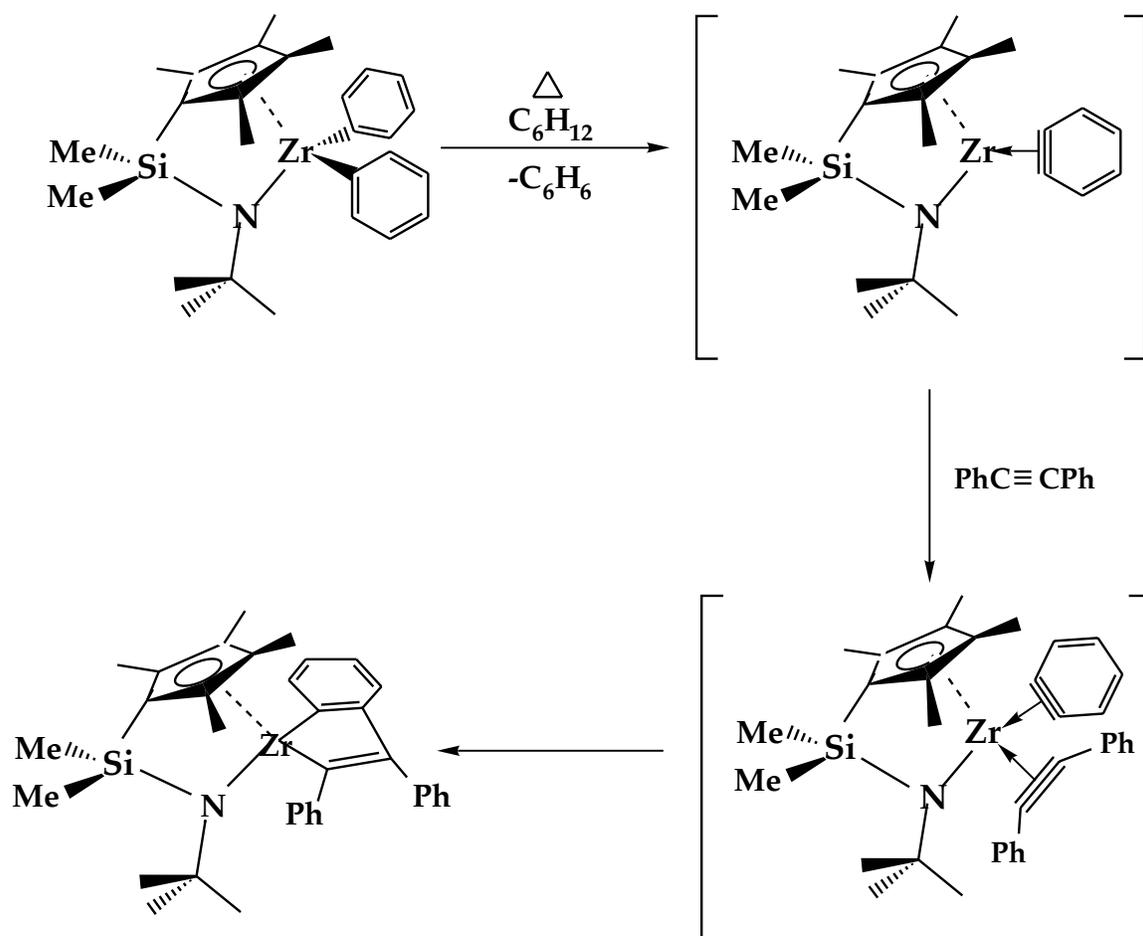
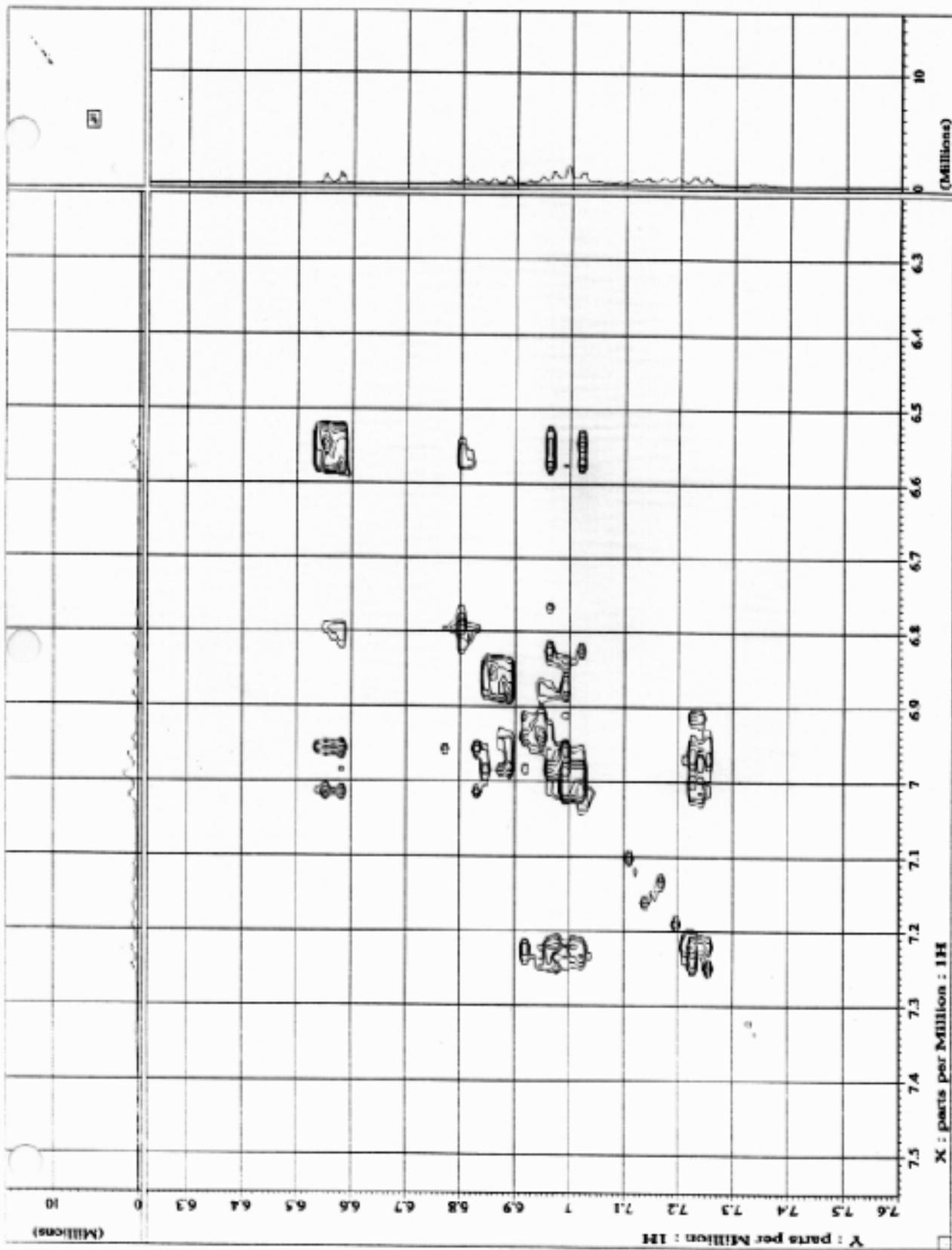


Figure 8. Coupling reaction of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ with diphenylacetylene.

Figure 9. 2D COSY NMR spectrum for
[(C₅Me₄)SiMe₂(N-t-Bu)]Zr[(C₆H₄)C(Ph)=C(Ph)].



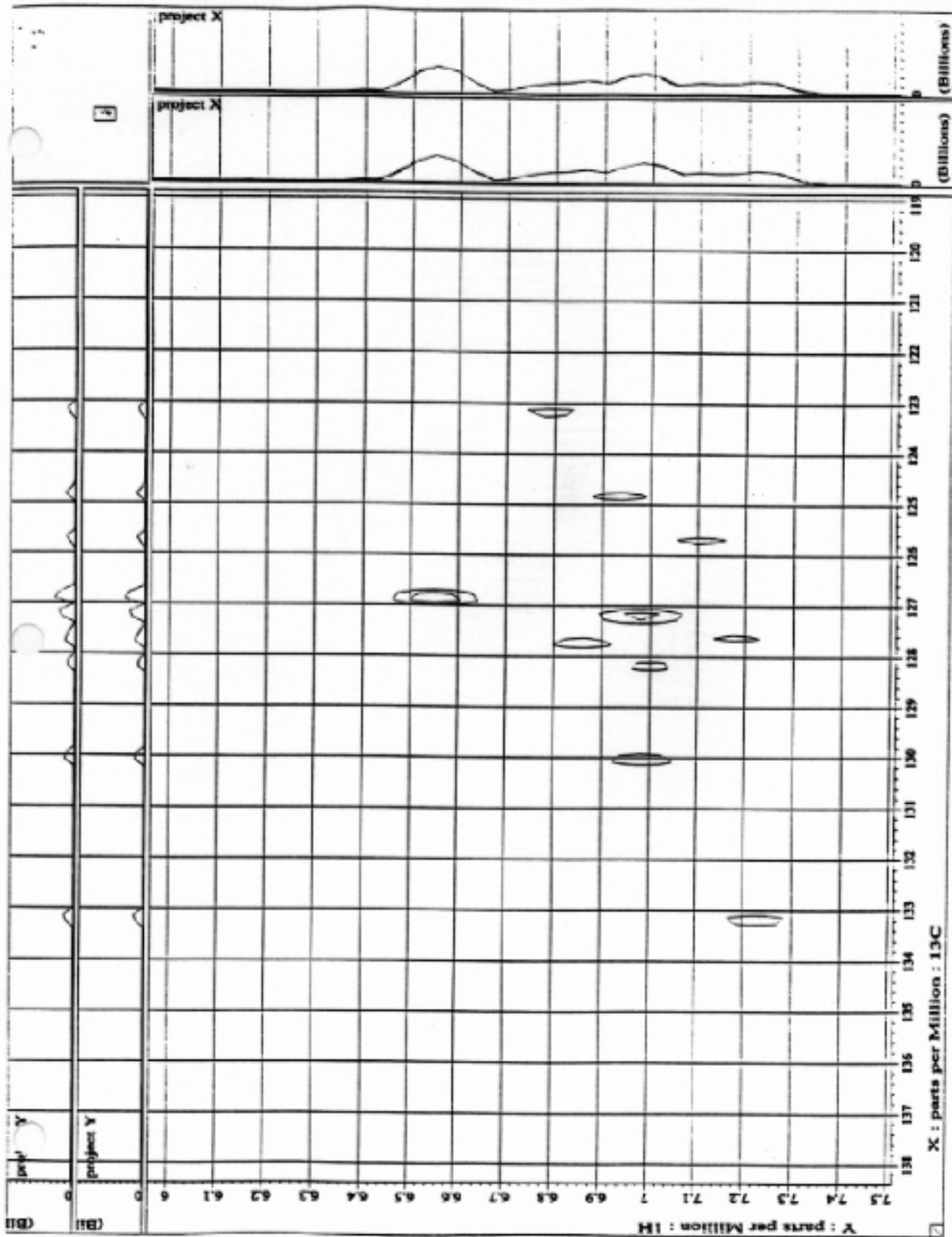
and 11.4. There is a signal at δ 97.4 representing the bridgehead carbon of the cyclopentadienyl ring and four resonances at δ 127.9, 128.6, 132.7, and 132.8 for the four remaining ring carbons. There are six signals for the benzyne functionality, with the peaks at δ 126.9, 123.2, 127.2, and 128.1 corresponding to the four carbon atoms with hydrogens leaving the two peaks at δ 146.3 and δ 186.7 assigned to the two quaternary carbons within the five-membered zirconacyclopentadiene ring. The two independent phenyl substituents exhibit eight carbon resonances. The peaks at δ 124.8, 125.7, 127.6, 127.8, 130.1, and 133.1 represent the *ortho*-, *meta*-, and *para*-carbons and the two resonances at δ 140.9 and δ 144.7 are due to the two ipso-quaternary carbons. The two signals at δ 150.5 and δ 197.2 correspond to the two remaining carbon atoms of the five-membered zirconacyclic ring.

Description of the Molecular Structure of [(C₅H₄)SiMe₂(N-t-Bu)]Ti[(C₆H₄)C(Ph)=C(Ph)].

The molecular structure of [(C₅H₄)SiMe₂(N-t-Bu)]Ti[(C₆H₄)C(Ph)=C(Ph)] was confirmed by an X-ray crystallographic analysis. This organotitanium compound crystallizes in a C-centered monoclinic lattice with 8 symmetry-related molecules within the unit cell. A perspective view of its molecular structure is shown in Figure 11 with the atom numbering scheme. Pertinent bond distances and angles are provided in Table 4. The molecular structure is well-behaved with no indications of a structural disorder or excessive thermal motion.

The most prominent feature in this structure is the titanacyclopentadiene ring constructed from the direct C-C coupling of a coordinated benzyne fragment with diphenylacetylene. This titanacyclic ring

Figure 10. 2D HETCOR NMR spectrum measured for
 $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[(C_6H_4)C(Ph)=C(Ph)]$.

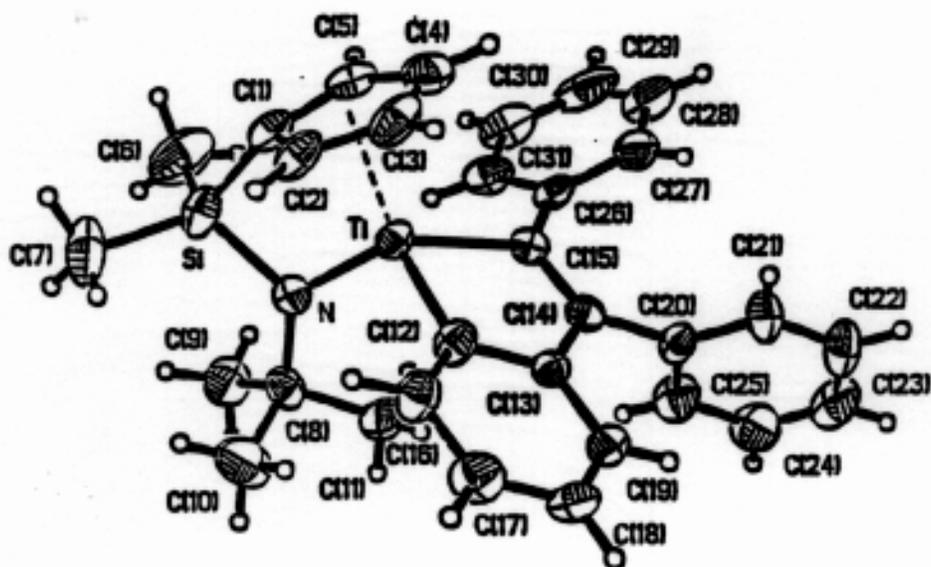


is essentially planar with the mean deviation for the Ti and four carbon atoms being 0.035 Å. The three independent C-C distances of 1.404(8), 1.511(8) and 1.355(8) Å are consistent with alternating localized C=C double bonds around the ring with the longer C=C bond being associated with the benzyne fragment. The five-membered titanacyclopentadiene ring and the six membered ring of the C₆H₄ fragment are essentially coplanar, with the acute dihedral angle between their respective planes being only 3.5°. To minimize interring repulsions, the two phenyl substituents containing carbon atoms C(20)-C(25) and C(26)-C(31) are rotated by 76.8° and 41.3°, respectively, out of the plane of the titanacyclopentadiene ring.

The asymmetric pseudo-tetrahedral coordination sphere consists of the π -bonded cyclopentadienyl ring and its appended amido functionality and two chemically inequivalent Ti-C bonds of 2.081(7) and 2.103(7) Å. These two distances are considerably shorter than the two independent Ti-C bonds of 2.172(5) and 2.141(5) Å reported by Atwood and co-workers³⁹ for the related planar titanacyclopentadiene ring of Cp₂Ti(C₄(Ph)₄), which was prepared by the photolysis of Cp₂TiMe₂ in the presence of diphenylacetylene. This observed difference in these two pairs of Ti-C bond distances is most likely a consequence of the increased electrophilicity associated with the electron deficient d⁰ Ti(IV) center arising from the presence of the bifunctional *ansa*-monocyclopentadienylamido ligand in [(C₅H₄)SiMe₂(N-t-Bu)]Ti[(C₆H₄)C(Ph)=C(Ph)], thus leading to a substantial shortening of both of its Ti-C bonds. The C(12)-Ti-C(15) bond angle of 85.1(3)° within the five membered titanacyclopentadiene ring of [(C₅H₄)SiMe₂(N-t-Bu)]Ti[(C₆H₄)C(Ph)=C(Ph)] is *ca.* 5° larger than the corresponding C-Ti-C angle in Cp₂Ti(C₄(Ph)₄). This increase is accompanied by a *ca.* 3° decrease in the Ti-C _{α} -C _{β} bond angles.

The presence of the SiMe₂ linkage between the cyclopentadienyl and amido functionalities of [(C₅H₄)SiMe₂(N-t-Bu)]Ti[(C₆H₄)C(Ph)=C(Ph)] produces a Cp(c)-Ti-N angle of 108.4°, which is only modestly larger than its corresponding value of 107.0° in [(C₅H₄)SiMe₂(N-t-Bu)]TiCl₂. The similarity of the respective Ti-N(amido) (1.915(5) and 1.901(3) Å) and Ti-Cp(c) (2.025 and 2.019 Å) for these two complexes indicates that these distances are relatively insensitive to the presence of the titanacyclopentadiene ring.

Figure 11. Perspective view of the molecular structure of
 $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$
with the non-hydrogen atom labeling scheme.



Concluding Remarks

The metathetical reaction of $[(C_5R_4)SiMe_2(N-t-Bu)]MCl_2$ with two equivalents of an appropriate phenylating reagent results in the formation of $[(C_5R_4)SiMe_2(N-t-Bu)]M(C_6H_5)_2$ ($R=H, Me$; $M=Ti, Zr$), which have been characterized by both 1H and ^{13}C NMR measurements. The utilization of a specific phenyl reagent is not general for the preparation of these diphenyl complexes, but is dependent on the choice of the dichloride precursor.

The stoichiometric reaction of $[(C_5H_4)SiMe_2(N-t-Bu)]TiCl_2$ with two equivalents of $PhMgBr$ produced $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$ in reasonable yield. The reaction of $[(C_5Me_4)SiMe_2(N-t-Bu)]ZrCl_2$ with two equivalents of $PhLi$ proceeded cleanly with the formation of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ in a relatively good yield. Upon treating $[(C_5H_4)SiMe_2(N-t-Bu)]ZrCl_2$ with two equivalents of $PhMgCl$, the desired product, $[(C_5H_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ was obtained. The isolation of $[(C_5H_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$, was hindered by its tendency to decompose within a few hours upon standing at ambient temperature. This color change was accompanied by deterioration of the NMR spectral features for $[(C_5H_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$.

Two of the diphenyl precursors, $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$ and $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$, were each separately reacted with one equivalent of diphenylacetylene in an effort to trap the benzyne intermediate and to isolate the resultant five membered metallacyclic product. The coupling reaction involving $[(C_5H_4)SiMe_2(N-t-Bu)]Ti(C_6H_5)_2$ and diphenylacetylene proceeded smoothly in cyclohexane at $80^\circ C$ with the formation of one primary product, $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$. The reaction of $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr(C_6H_5)_2$ with one equivalent of diphenylacetylene led to a product mixture from

which the desired product $[(C_5Me_4)SiMe_2(N-t-Bu)]Zr[(C_6H_4)C(Ph)=C(Ph)]$ was isolated. Each of these two products was characterized by both 1H and ^{13}C NMR along with COSY and HETCOR 2D NMR measurements.

The molecular structure of $[(C_5H_4)SiMe_2(N-t-Bu)]Ti[(C_6H_4)C(Ph)=C(Ph)]$ was confirmed by X-ray structural analysis. This compound exhibits an asymmetric pseudo-tetrahedral coordination sphere consisting of a bifunctional *ansa*-monocyclopentadienylamido chelate ligand and a π -bonded cyclopentadienyl ring. The two inequivalent Ti-C bond distances are considerably shorter than the two independent Ti-C bonds of $Cp_2Ti(C_4(Ph)_4)$ reported in the literature. The observed difference in these two pairs of Ti-C bond distances is most likely a consequence of the increased electrophilicity associated with the electron deficient d^0 Ti(IV) center arising from the presence of the bifunctional *ansa*-monocyclopentadienylamido ligand, leading to a substantial shortening of the two Ti-C bonds.

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Abstract

Upon thermolysis in aromatic solvents, diarylzirconacenes and diaryltitanocenes form benzyne intermediates. Formation of the benzyne intermediate presumably occurs via H-atom abstraction of an *ortho*-H of an aryl ligand by the adjacent σ -bonded aryl ligand to give the benzyne intermediate. The diphenylzirconocene benzyne intermediate can be stabilized by the addition of PMe_3 to afford the PMe_3 adduct which has been isolated and structurally characterized. This benzyne intermediate couples with a variety of unsaturated organic fragments including nitriles, alkenes, and acetylenes to form metallacyclic species and has found applications in organic synthesis. This benzyne also couples with tungsten hexacarbonyl to afford a Fischer-type metalloxycarbene complex.

Procedures for making the diphenyl precursors $[(\text{C}_5\text{R}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{M}(\text{C}_6\text{H}_5)_2$ ($\text{R}=\text{H, Me}$; $\text{M}=\text{Ti, Zr}$) were developed. Separate coupling reactions involving two of the diphenyl precursors $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Ti}(\text{C}_6\text{H}_5)_2$ and $[(\text{C}_5\text{Me}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Zr}(\text{C}_6\text{H}_5)_2$, with diphenylacetylene affords $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Ti}[(\text{C}_6\text{H}_4)\text{C}(\text{Ph})=\text{C}(\text{Ph})]$ and $[(\text{C}_5\text{Me}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Zr}[(\text{C}_6\text{H}_4)\text{C}(\text{Ph})=\text{C}(\text{Ph})]$, respectively. These compounds have been characterized by ^1H and ^{13}C NMR along with 2D COSY and HETCOR NMR measurements. The structure of $[(\text{C}_5\text{H}_4)\text{SiMe}_2(\text{N-t-Bu})]\text{Ti}[(\text{C}_6\text{H}_4)\text{C}(\text{Ph})=\text{C}(\text{Ph})]$ was also verified through X-ray structural analysis.

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Vita

The author is the son of Mr. and Mrs. R.A. Nettles, Sr. and was born on October 21, 1973 in Wheeling, West Virginia. He lived his entire childhood in nearby Benwood, West Virginia and graduated from Bishop Donahue Memorial High School, McMechen, West Virginia, in 1991. He received a Bachelor of Science degree in Chemistry from Wheeling Jesuit College, Wheeling, West Virginia in May 1995. He is currently a graduate student in the department of Chemistry at West Virginia University, Morgantown, West Virginia, where he is a candidate for the degree of Master of Science.

Approval of the Examining Committee

**SYNTHESIS AND CHARACTERIZATION OF ELECTROPHILIC
GROUP 4 METAL COMPLEXES OF BENZYNES**

By

Shawn M. Nettles

THESIS

Submitted to
The College of Arts and Sciences
at
West Virginia University
in partial fulfillment of the requirements
for the degree of
Master of Science
in
Chemistry

Robert S. Nakon, Ph.D.

Björn C. Söderberg, Ph.D.

Date

Jeffrey L. Petersen, PhD., Chairman

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