Synthesis, Structure, and Reactivity of Titanacyclopentadiene Complexes Bearing Ancillary Pyridine Diamide Ligands

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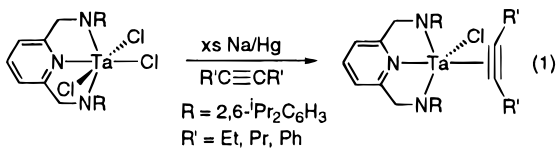
Titanium complexes bearing the pyridine diamide ligands $[2,6\text{-}(RNCH_2)_2NC_5H_3]^{2-}$ (R = 2,6-diisopropylphenyl (BDPP); R = 2,6-dimethylphenyl (BDMP)) have been synthesized. Reduction of the dichloride precursors (BDPP)$TiCl_2$ (**1a**) and (BDMP)$TiCl_2$ (**1b**) with excess 1% Na/Hg amalgam in the presence of >2 equiv of internal (PhC≡CPh, EtC≡CEt, PrC≡CPr) or terminal ($HC{\equiv}CSiMe_3$, PhC≡CH) alkynes yields metallacyclopentadiene derivatives in good yield. The α,β′-substituted titanacycle (BDPP)Ti$[C_4H_2(SiMe_3)_2]$ (**5a**) was characterized by X-ray crystallography and is best described as a distorted square pyramid with the metallacycle carbon C(4) occupying the apical position. The α,α′-substituted titanacycle (BDMP)Ti$[C_4H_2(SiMe_3)_2]$ (**5b**) reacts with excess 3-hexyne and 4-octyne to give the asymmetric metallacycles (BDMP)Ti$[C_4Et_2H(SiMe_3)]$ (**7b**) and (BDMP)Ti$[C_4Pr_2H(SiMe_3)]$ (**8b**), respectively. No cyclotrimerization of alkyne is observed. Ligand activation is observed in certain cases for complexes bearing the BDMP ligand.

Introduction

The organometallic chemistry of Ti(IV) has been dominated by complexes bearing cyclopentadienyl ligands.[1] There is, however, a growing interest in the use of alternative ligands such as alkoxides[2−6] and amides[7−11] which may be viewed as electron deficient cyclopentadienyl equivalents. In particular, titanium amide complexes have been shown to stabilize reactive species such as methylidene ligands,[12] and alkyl groups with β-hydrogens[13] and are precursors for both the highly active[14] and living polymerization[15] of α-olefins. Titanium complexes bearing multidentate diamide[16−22] and triamide[23−25] ligand systems take advantage of what is anticipated to be a relatively rigid stereoelectronic environment.

Metallacyclopentadiene complexes are key intermediates in a number of cyclization reactions,[26] for example, the catalytic cyclotrimerization of alkynes. Previously,[27] we have reported the synthesis and structure of alkyne derivatives of tantalum stabilized by a pyridine diamide ligand (eq 1).



(1)

Although these complexes serve as useful starting materials for studying the insertion of an alkyne into a

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(1) Bochmann, M. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science Ltd.: New York, 1995; Vol. 4, pp 273−431.
(2) Jones, R. A.; Hefner, J. G.; Wright, T. C. *Polyhedron* **1984**, *3*, 1124.
(3) Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977.
(4) Duff, A. W.; Kamarudin, R. A.; Lappert, M. F.; Norton, R. J. *J. Chem. Soc., Dalton Trans.* **1986**, 489.
(5) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guestini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66.
(6) Balaich, G. L.; Hill, J. E.; Waratuke, S. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1995**, *14*, 656 and references therein.
(7) Bürger, H.; Kluess, C. *J. Organomet. Chem.* **1976**, *108*, 69.
(8) Planalp, R. P.; Andersen, R. A.; Zalkin, R. A. *Organometallics* **1983**, *2*, 16.
(9) Bradley, D. C.; Chudzynska, H.; Backer-Dirks, J. D. J.; Hursthouse, M. B.; Ibrahim, A. A.; Motevalli, M.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 1423.
(10) Canich, J. A.; Turner, H. W. (Exxon) PCT Int. Appl. WO 92/12162, 1992.
(11) Johnson, A. R.; Cummins, C. C.; Davis, W. M. *Organometallics* **1996**, *15*, 3825.
(12) Scoles, L.; Minhas, R.; Duchateau, R.; Jubb, J.; Gambarotta, S. *Organometallics* **1994**, *13*, 4978.
(13) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452.
(14) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241.
(15) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008.
(16) Jones, R. A.; Seeberger, M. H.; Atwood, J. L.; Hunter, W. E. *J. Organomet. Chem.* **1983**, *247*, 1.
(17) tom Dieck, H.; Rieger, H. J.; Fendesak, G. *Inorg. Chim. Acta* **1990**, *177*, 191.
(18) Herrmann, W. A.; Denk, M.; Albach, R. W.; Behm, J.; Herdtweck, E. *Chem. Ber.* **1991**, *124*, 683.
(19) Friedrich, S.; Gade, L. H.; Edwards, A. J.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2861.
(20) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333.
(21) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562.
(22) Aoyagi, K.; Gantzel, P. K.; Kalai, K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923.
(23) Cummins, C. C.; Lee, J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.
(24) Schubart, M.; O'Dwyer, L.; Gade, L. H.; Li, W.; McPartlin, M. *Inorg. Chem.* **1994**, *33*, 3893.
(25) Schrock, R. R.; Cummins, C. C.; Wilhelm, T.; Lin, S.; Reid, S. M.; Kol, M.; Davis, W. M. *Organometallics* **1996**, *15*, 1470.
(26) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapters 9 and 18.
(27) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 3154.

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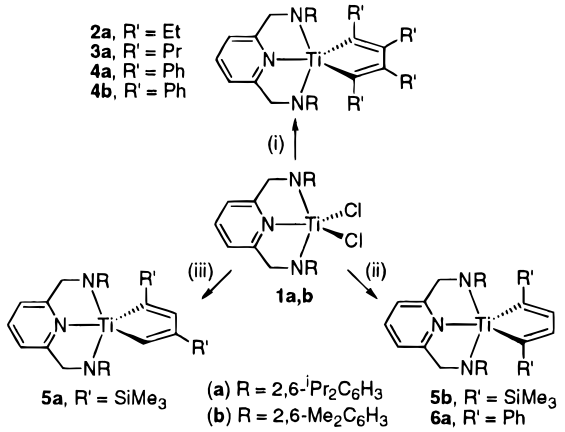
Scheme 1. Preparation of Titanacyclopentadiene Derivatives[a]



[a] Reagents and conditions: toluene, 23 °C, excess Na/Hg amalgam, >2 equiv alkyne; (i) R′C≡CR′, R′ = Et, Pr, Ph; (ii) R′C≡CH, R′ = $SiMe_3$, Ph; (iii) R′C≡CH, R′ = $SiMe_3$.

metal−carbon bond,[28] the coupling of two alkynes to give a tantalacyclopentadiene derivative is thwarted by the presence of the remaining apical chloride ligand. As a result, we decided to investigate the intramolecular coupling of alkynes at a reduced titanium center; for example, via the reduction of the known dichloride precursor [2,6-$(RNCH_2)_2NC_5H_3$]$TiCl_2$ (R = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-$Me_2C_6H_3$).[29] In this paper we report a series of titanacyclopentadiene derivatives containing pyridine diamide ligands. The preparation and reactivity of these new compounds is compared to metallacyclic analogues bearing the fragments Cp_2Ti[30] and $(RO)_2Ti$.[31]

Results

The titanacyclopentadiene complexes **2a**−**4a**,**4b** were prepared by the reduction of the dichloride precursors (BDPP)$TiCl_2$ (**1a**, BDPP = 2,6-$(R'NCH_2)_2NC_5H_3$, R′ = 2,6-^{i}Pr$_2$C$_6$H$_3$) and (BDMP)$TiCl_2$ (**1b**, BDMP = 2,6-$(R'NCH_2)_2NC_5H_3$, R′ = 2,6-$Me_2C_6H_3$)[29] with excess 1% Na/Hg amalgam in toluene at 23 °C in the presence of >2 equiv of alkyne (Scheme 1). Orange-red solutions of the dichlorides **1a,b** slowly become dark red-brown over 12 h. Filtration of the crude toluene solutions and recrystallization from pentane affords the titanacyclic products in good yield (∼65%). Although the metallacyclic products **2b** and **3b** (not shown) were observed by ^{1}H NMR spectroscopy, they proved too soluble to separate from the byproducts in the reaction (*vide infra*). The aryloxide supported titanacycle (Ar″O)$_2$Ti(C_4Ph_4) (Ar″ = 2,6-$Ph_2C_6H_3$) cannot be obtained via the reduction of the dichloride precursor (Ar″O)$TiCl_2$.[31] In contrast, the metallacycles **4a,b** are obtained in ∼65% yield, which suggests that the pyridine diamide ligand plays an important role in stabilizing reduced titanium intermediates. Metallacycles **2a**−**4a**,**b** do not react further with additional alkyne even at elevated temperatures (110 °C, 24 h).

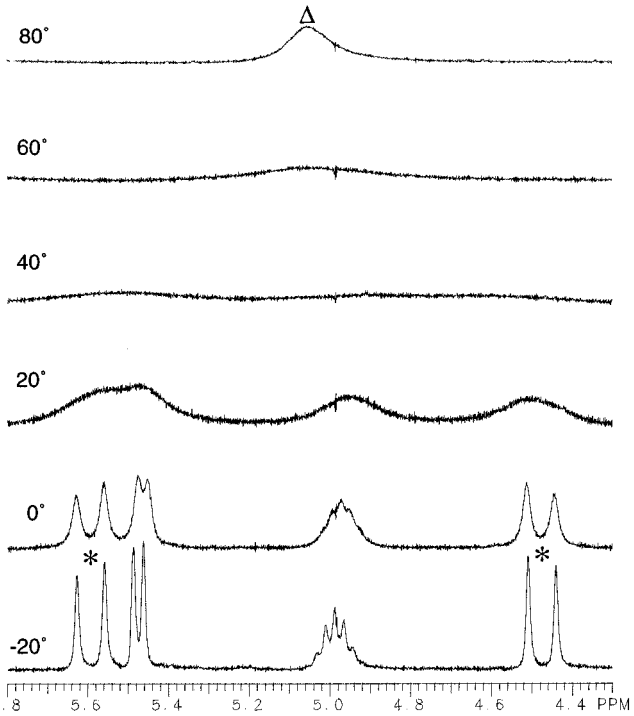
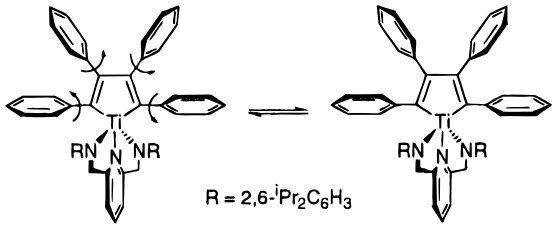


Figure 1. Variable-temperature proton NMR spectra of the ligand methylene (CH_2N) region of compound **4a**.

Scheme 2



The proton NMR spectra of complexes **2a**, **3a**, and **4b** show a singlet for the ligand methylene protons (NCH_2), consistent with meridional coordination of the pyridine diamide ligand. The carbon spectra of compounds **2a**−**4a**,**b** show characteristic[30,31] low-field resonances (>190 ppm) for the α-carbons of the metallacycle. The ^{1}H NMR spectra of compounds **2a** and **3a** display chemically inequivalent ethyl and propyl substituents (α and *β*) for the titanacycles. The ^{1}H NMR spectrum of compound **4a**, however, is quite broad at 23 °C. A stacked plot of the ligand methylene (CH_2N) region of compound **4a** at various temperatures is shown in Figure 1.

As the temperature is increased, the resonance at about 5.47 ppm (C−*H o*-phenyl) shifts to lower field while the resonances at 4.99 ppm ($CHMe_2$) and 2.79 ppm ($CHMe_2$—not shown) coalesce to a single resonance at 3.88 ppm. The high temperature limiting spectrum (80 °C) shows a single broad resonance (Δ) for the methylene protons at about 5.05 ppm. The low temperature limiting spectrum (−20 °C) shows an AB quartet ($^2J_{HH}$ = 20.63 Hz) for the methylene protons (*). We interpret this exchange process to the restricted rotation ($\Delta G^{\ddagger}$ = 14.7(5) kcal mol^{-1}) of the phenyl rings of the titanacycle (Scheme 2).

The bulky 2,6-diisopropylphenyl substituents on the amide nitrogens prevent free rotation of the phenyl rings in the α and α′ positions which in turn affects the orientation of the phenyl groups in the *β* and *β*′ positions

(28) Guérin, F.; McConville, D. H.; Vittal, J. J. Manuscript in preparation.
(29) Guérin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, 15, 5085.
(30) Alt, H. G.; Englehardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Am. Chem. Soc.* **1985**, *107*, 3717.
(31) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911.

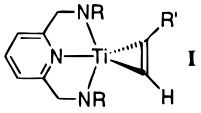
Table 1. Summary of Crystallographic Data, Collection Parameters, and Refinement Parameters for Compound 5a[a]

empirical formula	$C_{41}H_{61}N_3Si_2Ti_1$
fw	700.01
cryst color, habit	orange, plate
cryst dimens (mm)	0.38 × 0.34 × 0.18
cryst system	monoclinic
reflcns used for unit cell determination (2θ range (deg))	23 (18.2−22.6)
a (Å)	10.630(3)
b (Å)	36.650(9)
c (Å)	12.200(4)
β (deg)	110.73(2)
V (Å^3)	4445(2)
space group	$P2_1/n$
Z	4
ρ (calc) (g/mol)	1.046
collcn temp (°C)	25
F_{000}	1512
Mo Kα	graphite (monochromated)
scan mode	ω (variable 2−20 deg/min)
tot. no. of unique reflcns	6646
no. of observns with $F_0 \geq 4\sigma(F_0)$	5362
no. of variable params	258
$R1$[a]	0.102
w$R2$[a]	0.203
goodness of fit (GooF)[a]	0.996

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; w$R2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; GooF $= [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (where n is the number of reflections and p is the number of parameters refined).

of the titanacycle. Thus, the low temperature limiting structure would have C_2 symmetry while the high temperature limiting structure would have C_{2v} symmetry. The solid-state structure of $Cp_2Ti(C_4Ph_4)$ shows a propeller arrangement of the phenyl rings as proposed here.[32]

Terminal alkynes reacts with the dichlorides **1a,b** under reducing conditions to yield the metallacycles **5a,b** and **6a**. Assuming that compounds **5a,b** and **6a** proceed through a common mono(alkyne) intermediate (**I**), the regiochemistry of the insertion of the second alkyne can be rationalized in the following way:



I

Back-side attack of the second alkyne to intermediate **I** is hindered by the R′ substituent (Ph or $SiMe_3$). Thus, when the pyridine diamide ligand bears the larger 2,6-diisopropylphenyl substituents at nitrogen and the incoming alkyne is bulky (HC≡CSiMe$_3$), the bulk of this alkyne is directed away from the isopropyl groups of the ligand to give the α,β′ product (**5a**). When the incoming alkyne is relatively small (HC≡CPh), the more favorable α,α′ product is obtained (**6a**). In contrast, for the less sterically demanding 2,6-dimethylphenyl substituted ligand, the second alkyne inserts with the R′ substituent directed toward the ligand, resulting in the α,α′ isomer (**5b**). For comparison, $Cp_2Ti(C_4H_2Ph_2)$ display the α,β′ regiochemistry while $Cp_2Ti(C_4H_2Me_2)$ displays the α,α′ regiochemistry, reflecting the difference in steric bulk of the two alkynes.[32] Compounds **5a,b** and **6a** do not isomerize when heated to 80 °C in benzene.

The solid-state structure of **5a** was determined by X-ray crystallography (Table 1). The molecular structure of complex **5a** can be found in Figure 2, and relevant bond distances and angles, in Table 2. The structure is best described as a distorted square pyramid with the metallacycle carbon C(4) occupying the apical position. The alternating short−long−short bond distances in the titanacycle are consistent with its diene formulation. The titanium atom lies about 0.45 Å above the basal plane defined by the three nitrogens and C(1). The Ti−amide distances are comparable to the Ti−amide distances in the square pyramidal complex (BDMP)TiBr(CH_2CMe_2Ph) (1.979(5) and 1.977(6) Å).[29] The rigid coordination of the ligand and enforced location of the aryl isopropyl groups necessarily protect the metal above and below the N_3 plane. In fact, the congested environment about the titanium may in part explain the lack of insertion chemistry associated with this complex (*vide infra*).

The aryloxide complex $(Ar''O)_2Ti(C_4Et_4)$ is a catalyst for the cyclotrimerization of alkynes.[31] In contrast, there are no reports of alkyne cyclization catalyzed by titanacyclopentadiene derivatives of the type $Cp_2Ti(C_4R_4)$. Although compounds **2a**, **4b**, and **5a** do not react

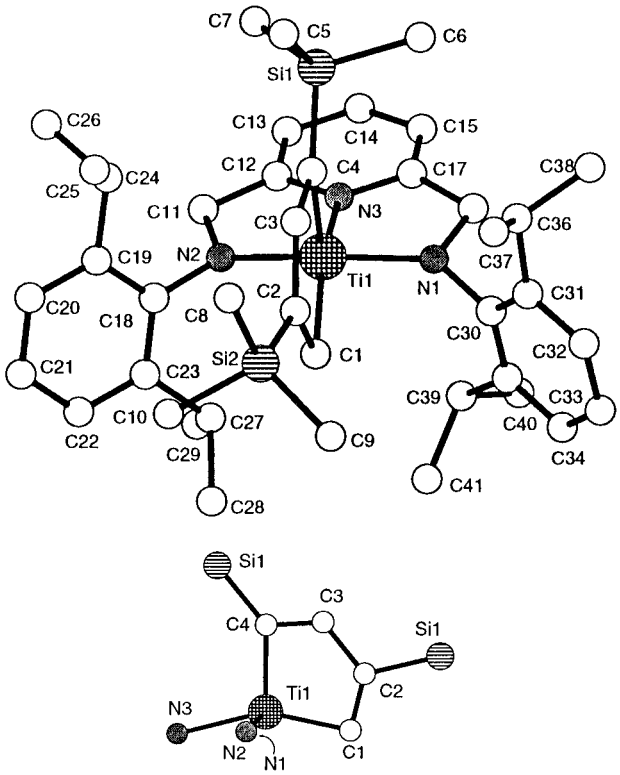


Figure 2. Top: Chem 3D representation of the molecular structure of **5a**. Bottom: Chem 3D representation of the core of **5a**.

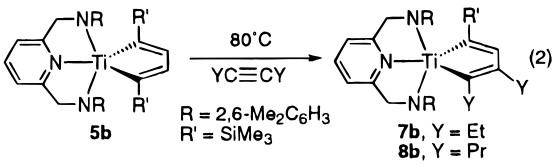
Table 2. Selected Bond Distances (Å) and Angles (deg) for 5a

Bond Distances			
Ti(1)−C(1)	2.046(11)	Ti(1)−C(4)	2.070(10)
Ti(1)−N(1)	1.989(8)	Ti(1)−N(2)	2.009(8)
Ti(1)−N(3)	2.172(8)	C(1)−C(2)	1.348(13)
C(2)−C(3)	1.553(14)	C(3)−C(4)	1.357(13)

Bond Angles			
N(2)−Ti(1)−N(3)	74.1(3)	C(1)−Ti(1)−C(4)	100.7(4)
N(2)−Ti(1)−N(1)	141.5(3)	N(3)−Ti(1)−N(1)	73.6(3)
Ti(1)−N(3)−C(1)	155.6(4)	Ti(1)−N(3)−C(4)	103.6(4)
C(30)−N(1)−C(17)	109.8(7)	C(18)−N(2)−C(11)	112.3(7)
C(17)−N(1)−Ti(1)	121.8(6)	Ti(1)−N(2)−C(11)	122.1(6)
Ti(1)−N(1)−C(30)	128.3(6)	Ti(1)−N(2)−C(18)	125.3(6)

(32) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454.

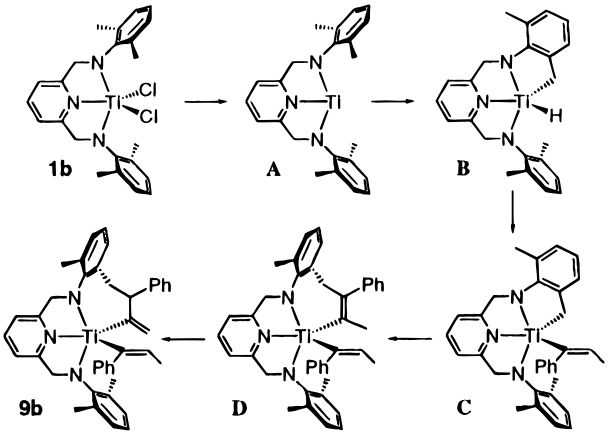
with alkynes (110 °C, 24 h), compound **5b** reacts with excess alkyne at 80 °C to give the asymmetric metallacycle derivatives **7b** and **8b** in quantitative yield by ^{1}H NMR spectroscopy (eq 2).



The regiochemistry of the metallacycle (α, β, α′) in compound **7b** was assigned on the basis of NOE experiments. For example, irradiation of the methylene signal of the ethyl group in the β-position (2.14 ppm) caused an enhancement of the metallacycle proton at 8.23 ppm, confirming the proximity of these two groups (irradiation of other groups was consistent with this assignment). Fragmentation of a metallacycle to an intermediate bis(alkyne) derivative has been proposed to explain the substitution of the alkynes in $(Ar''O)_2Ti(C_4Et_4)$.[31,33] In addition, disruption of the metallacycle to a mono(alkyne) adduct and free alkyne has been proposed for alkyne exchange in tantalum alkoxide systems.[34] Although we can not distinguish between these mechanism at present, it is interesting that only one of the alkynes is displaced. We are currently exploring the scope and mechanism of this transformation.

As noted above, the reduction of $(BDMP)TiCl_2$ in the presence of 3-hexyne or 4-octyne yields an inseparable mixture of the corresponding titanacycle and a byproduct. In the presence of >2 equiv of MeC≡CPh, however, the byproduct (**9b**) is formed in high yield and is easily separable from small amounts of the metallacycle. Proton and carbon NMR spectra clearly show the presence of a vinyl moiety likely derived from the insertion of MeC≡CPh into a Ti−H bond (−PhC═CHMe). Curiously, only three aryl methyl resonances are observed for the BDMP ligand. C_1 symmetry can be assigned to complex **9b** on the basis of the presence of separate resonances for all four ligand methylene protons (NCH_2). Using a combination of ^{1}H homonuclear decoupling and ^{1}H−^{13}C correlation spectroscopy experiments, the proposed structure of this complex and a possible mechanism for its formation are shown in Scheme 3. Reduction of the dichloride **1b** yields an intermediate Ti(II) complex (**A**) which activates the methyl group of the arene. Presumably this does not occur at any significant rate during the reduction of complex **1a** since the methine proton is well protected by the isopropyl methyls. The newly formed alkyl−hydride complex (**B**) inserts MeC≡CPh to give the observed vinyl moiety as shown in **C**. The regiochemistry of the insertion is based on the observed coupling between the vinylic C−H and the methyl group (6.2 Hz). Insertion of a second equivalent of MeC≡CPh into the Ti−C bond formed via the metalation (**D**), followed by a 1,3-hydrogen shift, yields the final product **9b**. The proton shift may occur in an attempt to relieve ring strain. Attempts to prepare an authentic Ti(II) complex (e.g., $(BDMP)TiL_2$, L = phosphine) have been unsuccessful. It is not clear why this ligand-activated complex forms in such high yield for certain alkynes; for example, we see no evidence of ligand metalation when compound **1b** is reduced in the presence of diphenylacetylene.

Scheme 3. Proposed Mechanism for the Formation of 9b



Conclusions

Pyridine diamide complexes of titanium can be reduced in presence of internal and terminal alkynes to give the corresponding metallacyclopentadiene derivatives in good yield. The titanacycles **2a**−**4a**,**b**, **5a**, and **6a** do not react further with excess alkyne. The α,α′-substituted metallacycle $(BDMP)Ti[C_4(SiMe_3)_2]$ reacts with excess alkyne via an apparent bis(alkyne) intermediate to give an unusual mixed titanacycle; the symmetrical metallacycles ($L_nTiC_4R_4$, R = Et, Pr) are not observed. Activation of the aryl methyl group of the BDMP ligand appears to compete with metallacycle formation in certain cases. The BDPP ancillary which bears 2,6-diisopropylphenyl substituents at nitrogen is not activated under the conditions studied; however, the steric bulk of this ligand precludes further reaction of the metallacycles. The next generation of pyridine diamide ligands (alkyl substituents at nitrogen) which are less bulk and less susceptible to activation may provide a more useful stereochemical environment for these derivatives.

Experimental Section

General Details. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in an Innovative Technology Inc. glovebox. Solvents were distilled from sodium/benzophenone ketyl (DME, THF, hexanes, diethyl ether, and benzene) or molten sodium (toluene) under argon and stored over activated 4 Å molecular sieves. Phenylacetylene, diphenylacetylene, 1-phenylpropyne, 3-hexyne, 4-octyne, and (trimethylsilyl)acetylene were purchased from Aldrich and distilled prior to use. The complexes $(BDPP)TiCl_2$ (**1a**) and $(BDMP)TiCl_2$ (**1b**) were synthesized by a literature method.[29] Unless otherwise specified, proton (300 MHz) and carbon (75.46 MHz) NMR spectra were recorded in C_6D_6 at approximately 22 °C on a Varian Gemini-300 spectrometer. The proton chemical shifts were referenced to internal C_6D_5H (δ = 7.15 ppm), and the carbon resonances to C_6D_6 (δ = 128.0 ppm). Some carbon resonances are obscured by C_6D_6 and/or are overlapping. The elemental analysis were performed using sealed tin cups on a Fisons Instruments Model 1108 elemental analyzer by Mr. Peter Borda of this department.

(33) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211.
(34) Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275.

(BDPP)Ti(C_4Et_4) (2a). A toluene (30 mL) solution of compound **1a** (0.100 g, 0.174 mmol) and 3-hexyne (0.035 g, 0.426 mmol) was added to an excess of 1% Na/Hg amalgam (0.074 g of Na, 3.22 mmol; 7.40 g of Hg). The mixture was stirred for 12 h. The solution was decanted from the amalgam and filtered through a medium-porosity frit with the aid of Celite. The solvent was removed in *vacuo* to yield an orange-brown solid. Due to its high solubility, compound **2a** was not isolated in crystalline form (>95% yield by ^{1}H NMR): ^{1}H NMR 7.25−7.10 (m, 6H, Ar), 6.93 (t, 1H, py), 6.48 (d, 2H, py), 5.02 (s, 4H, NCH_2), 3.62 (sept, 4H, CHMe$_2$), 2.13 (m, 8H, α,β CH_2-Me), 1.35 (d, 12H, CHMe_2), 1.28 (d, 12H, CHMe_2), 0.92 and 0.39 (t, 6H each, α,β CH$_2$$Me$); ^{13}C{^{1}H} NMR δ 229.33 (C$_α$), 162.35, 154.12, 143.72, 137.97, 124.90, 123.78, 116.65, 68.72 (NCH_2), 28.86, 28.37, 28.16, 26.73, 24.49, 24.29, 22.20, 15.96.

(BDPP)Ti(C_4Pr_4) (3a). The preparation of compound **3a** is identical to that for **2a**. Compound **1a** (0.250 g, 0.435 mmol), 4-octyne (0.120 g, 1.09 mmol), and excess 1% Na/Hg amalgam (0.30 g, 13.0 mmol; 30.0 g Hg) gave dark red **3a** (0.213 g, 0.294 mmol, 68%) when recrystallized from diethyl ether at −30 °C: ^{1}H NMR 7.25−7.10 (m, 6H, Ar), 6.93 (t, 1H, py), 6.46 (d, 2H, py), 5.05 (br s, 4H, NCH_2), 3.64 (br sept, 4H, CHMe$_2$), 2.21 and 2.11 (m, 8H, α,β CH_2CH$_2$Me), 1.38 (d, 12H, CHMe_2), 1.24 (d, 12H, CHMe_2), 0.90 (m, 12H, α,β CH$_2$CH$_2$$Me$), 0.71 (br m, 8H, α,β CH$_2$CH_2Me); ^{13}C{^{1}H} NMR δ 229.33 (C$_α$), 162.22, 154.06, 143.80, 137.86, 124.94, 123.80, 116.57, 68.69 (NCH_2), 68.73, 39.09, 32.35, 28.42, 26.71, 25.05, 24.38, 23.25, 15.24. Anal. Calcd for $C_{47}H_{69}N_3Ti$: C, 77.97 ; H, 9.61; N, 5.80. Found: C, 78.18; H, 9.49; N, 6.20.

(BDPP)TiC_4Ph_4 (4a). The preparation of compound **4a** is identical to that for **2a**. Compound **1a** (0.500 g, 0.870 mmol), diphenylacetylene (0.310 g, 1.74 mmol), and excess 1% Na/Hg amalgam (0.60 g, 26.1 mmol; 60.0 g Hg) gave red crystalline **4a** (0.423 g, 0.620 mmol, 71%) when recrystallized from diethyl ether at −30 °C: ^{1}H NMR (23 °C) δ 7.2−6.1 (br m, Ar, Ph, py), 6.27 (d, 2H, py), 5.56 (br m, 2H, CH_2N), 4.95 (br m, 2H, CHMe$_2$), 4.51 (br m, 2H, CH_2N), 2.83 (br m, 2H, CHMe$_2$), 1.87 (br m, 6H,CHMe_2), 1.53 (br m, 6H, CHMe_2), 0.87 (br m, 12H, CHMe_2). ^{1}H NMR (−20 °C, toluene-d_8) δ 7.4−6.5 (m, Ar, Ph and py), 6.22 (d, py, 2H), 5.47 (d, 2H, Ph$_o$), 5.03 (AB quartet, $^2J_{HH}$ = 20.63 Hz, 4H, NCH_2), 4.99 (sept, 2H, CHMe$_2$), 2.79 (sept, 2H, CHMe$_2$), 1.93 (d, 6H, CHMe_2), 1.62 (d, 6H, CHMe_2), 0.91 (d, 6H, CHMe_2), 0.82 (d, 6H, CHMe_2); ^{13}C{^{1}H} NMR (−40 °C, toluene-d_8) δ 161.16, 152.28, 146.88, 138.03, 131.89, 131.60 (br), 131.78, 129.95, 127.27, 126.57, 126.17, 125.74, 124.23 (br), 123.19, 116.59, 69.21, 29.75 (br), 28.40 (br), 27.26 (br), 25.84 (br), 23.75. Anal. Calcd for $C_{59}H_{61}N_3Ti$: C, 82.40; H, 7.15; N, 4.89. Found: C, 82.37; H, 7.21; N, 5.13.

(BDMP)TiC_4Ph_4 (4b). The preparation of compound **4b** is identical to that for **2a**. Compound **1b** (0.500 g, 1.08 mmol), diphenylacetylene (0.482 g, 2.70 mmol), and excess 1% Na/Hg (0.25 g, 10.9 mmol; 24.9 g Hg) gave red crystalline **4b** (0.497 g, 0.665 mmol, 62%) when recrystallized from diethyl ether at −30 °C: ^{1}H NMR δ 7.21(d, 4H, Ar), 7.08 (t, 2H, Ar), 6.92 (m, 4H, Ph), 6.76 (m, 8H, Ph), 6.66 (m, 5H, Ph and py), 6.34 (d, 2H, py), 5.96 (m, 4H, Ph), 4.71 (s, 4H, CH_2N), 2.52 (s, 12H, Me); ^{13}C {^{1}H} NMR δ 221.66 (C$_α$), 161.72, 153.74, 146.02, 143.66, 140.22, 137.99, 134.07, 131.91, 130.48, 129.25, 127.08, 126.98, 125.80, 125.36, 123.31, 116.88, 66.16 (NCH_2), 19.24.

(BDPP)Ti[C_4H_2(SiMe_3)$_2$] (5a). The preparation of compound **5a** is identical to that for **2a**. Compound **1a** (0.200 g, 0.348 mmol), Me$_3$SiC≡CH (0.088 g, 0.696 mmol), and excess 1% Na/Hg amalgam (0.240 g of Na, 10.4 mmol; 24.0 g of Hg) gave yellow crystalline **5a** (0.157 g, 0.224 mmol, 64%) when recrystallized from pentane at −30 °C: ^{1}H NMR δ 8.68, 8.66 (s, 1H each, α,β′-CH), 7.15−7.05 (m, 6H, Ar), 6.95 (t, 1H, py), 6.53 (d, 2H, py), 4.92 (AB quartet, $^2J_{HH}$ = 21.15, 4H, NCH_2), 3.66 (sept, 2H, CHMe$_2$), 3.46 (sept, 2H, CHMe$_2$), 1.43 (d, 6H, CHMe_2), 1.28 (d, 6H, CHMe_2), 1.24 (d, 6H, CHMe_2), 1.15 (d, 6H, CHMe_2), 0.04 and −0.15 (s, 9H each, α,β′-SiMe_3); ^{13}C{^{1}H} NMR δ 218.81 (α-CH), 215.04 (α-CSiMe$_3$), 163.12, 153.33, 144.06, 142.71, 138.14 (β-CH), 137.63, 128.59, 124.94, 124.20, 123.64, 117.25, 67.35, 28.72, 27.10, 26.65, 26.41, 24.87, 23.78, −0.38, −1.86. Anal. Calcd for $C_{41}H_{61}N_3Si_2Ti$: C, 70.35; H, 8.78; N, 6.00. Found: C, 69.97; H, 8.94; N, 6.02.

(BDMP)Ti[C_4H_2(SiMe_3)$_2$] (5b). The preparation of compound **5b** is identical to that for **2a**. Compound **1b** (0.100 g, 0.216 mmol), Me$_3$SiC≡CH (0.047 g, 0.476 mmol), and excess Na/Hg amalgam (0.074 g of Na, 3.22 mmol; 7.40 g of Hg) gave yellow crystalline **5b** (0.431 g, 0.609 mmol, 70%) when recrystallized from pentane at −30 °C: ^{1}H NMR δ 8.50 (s, 2H, β,β′-CH), 7.03 (d, 4H, Ar), 6.94 (t, 1H, py), 6.91 (m, 2H, Ar), 6.55 (d, 2H, py), 4.59 (s, 4H, NCH_2), 2.27 (s, 12H, Me), −0.23 (s, 18H, α,α′-SiMe_3). ^{13}C{^{1}H} NMR δ 228.41 (CSiMe$_3$), 163.15, 156.02, 138.25, 133.72, 132.26, 124.70, 117.43, 65.45, 20.10, −0.28. Anal. Calcd for $C_{33}H_{45}N_3Si_2Ti$: C, 67.43; H, 7.72; N, 7.15. Found: C, 67.83; H, 7.93; N, 7.29.

(BDPP)Ti[$C_4H_2Ph_2$] (6a). The preparation of compound **6a** is identical to that for **2a**. Compound **1a** (0.500 g, 0.870 mmol), phenylacetylene (0.267 g, 2.61 mmol), and excess Na/Hg amalgam (0.60 g, 26.0 mmol; 60.0 g Hg) gave dark-red crystalline **6a** (0.431 g, 0.609 mmol, 70%) when isolated from diethyl ether at −30 °C: ^{1}H NMR δ 7.45 (s, 2H, β,β′-CH), 7.21 (m, 6H, Ar), 7.00 (t, 4H, Ph), 6.89 (m, 3H, Ph and py), 6.41 (d, 2H, py), 6.18 (d, 4H, Ph), 4.99 (s, 4H, NCH_2), 2.65 (sept, 4H, CHMe$_2$), 1.18 (d, 12H, CHMe_2), 1.20 (d, 12H, CHMe_2); ^{13}C{^{1}H} NMR δ 220.77 (α-CPh), 161.88, 153.74, 148.02 (β-CH), 143.50, 138.18, 125.65, 125.39, 125.25, 124.46, 124.16, 117.23, 68.32, 28.04, 26.70, 23.37. Anal. Calcd for $C_{47}H_{53}N_3Ti$: C, 79.75; H, 7.55; N, 5.94. Found: C, 79.35; H, 7.91; N, 5.99.

(BDMP)Ti[C_4Et_2H(SiMe_3)] (7b). A benzene (5 mL) solution containing complex **5b** (0.025g, 0.043 mmol) and 3-hexyne (0.030g, 0.365 mmol) was heated to 80 °C for 12 h. The solvent was removed in *vacuo* and the sample dissolved in C_6D_6. A quantitative yield was determined by ^{1}H NMR. ^{1}H NMR δ 8.23 (s, 1H, β′-CH), 7.05−6.95 (m, 5H, Ar and py), 6.88 (t, 2H, Ar), 6.55 (d, 2H, py), 4.65 (AB quartet, $^1J_{HH}$ = 21.1 Hz, CH_2N), 2.28 (s, 12H, Me), 2.14 and 1.89 (q, 2H each, CH_2Me), 0.87 and 0.27 (t, 3H each, CH$_2$$Me$), −0.08 (s, 9H, Si$Me_3$); ^{13}C{^{1}H} NMR δ 228.35, 221.93, 162.96, 155.30, 137.74, 135.44, 134.60, 134.00, 132.73, 123.88, 117.01, 64.99, 31.87, 27.82, 19.84, 19.11, 12.80, 12.63, −0.38.

(BDMP)Ti[C_4Pr_2H(SiMe_3)] (8b). A benzene (5 mL) solution containing complex **5b** (0.025g, 0.043 mmol) and 4-octyne (0.030g, 0.272 mmol) was heated to 80 °C for 12 h. The solvent was removed in *vacuo* and the sample dissolved in C_6D_6. A quantitative yield was determined by ^{1}H NMR. ^{1}H NMR δ 8.29 (s, 1H, β′-CH), 7.10−6.95 (m, 5H, Ar and py), 6.90 (t, 2H, Ar), 6.57 (d, 2H, py), 4.66 (AB quartet, $^2J_{HH}$ = 21.1 Hz, CH_2N), 2.30 (s, 12H, Me), 2.8 and 1.85 (m, 2H each, CH_2CH$_2$Me, 1.38 (m, 2H, CH$_2$CH_2Me), 0.82 and 0.70 (t, 3 each, CH$_2$CH$_2$$Me$), 0.58 (m, 2H, CH$_2CH_2$Me), −0.07 (s, 9H, Si$Me_3$); ^{13}C{^{1}H} NMR δ 228.64, 221.78, 162.95, 155.36, 137.78, 134.66, 133.90, 132.84, 129.25, 127.24, 127.04, 124.76, 123.95, 122.24, 120.20, 117.03, 65.18,41.40, 37.94, 22.04, 21.64, 19.86, 19.08, 15.28, 14.68, −0.34.

(BDMP′)Ti(MeCCPh)$_2$ (9b). A THF (30 mL) solution of compound **1b** (0.500 g, 1.08 mmol) and 1-phenylpropyne (0.314 g, 2.70 mmol) was added to an excess of Mg (0.250 g, 10.3 mmol). The mixture was stirred for 12 h. The solution was decanted from the magnesium and filtered through Celite. The solvent was removed in *vacuo* to yield a dark brown solid. The solid was dissolved in a minimum amount of diethyl ether and cooled to −30 °C for 12 h. Dark red crystalline **9b** was isolated by filtration and dried under vacuum (0.371 g, 0.595 mmol, 55%): ^{1}H NMR δ 7.20−6.80 (m, 15H, Ph, Ar and py), 6.63 and 6.41 (d, 1H each, py), 6.19 (m, 2H, Ph), 4.96 (AB quartet, $^2J_{HH}$ = 21.3 Hz, 2H, CH_2N), 4.71 (AB quartet, $^2J_{HH}$ = 19.9 Hz, 2H CH_2N), 3.65 (q, 1H, C=CHMe), 3.13 (m, 2H), 2.78 (m, 2H), 2.40 (s, 3H, ArMe), 1.97 (d, 3H, C=CHMe), 1.85 (m, 1H), 1.82 (s, 3H, ArMe), 0.94 (s, 3H, ArMe); ^{13}C{^{1}H} δ 166.32, 162.63, 154.66, 148.25, 147.98, 142.48, 141.40, 140.49, 137.30, 136.85, 135.47, 131.20, 129.01, 128.73, 127.44, 147.21, 126.93, 126.82, 126.53, 126.00, 122.62, 121.81, 120.62, 117.51, 117.09, 84.78,

71.57, 69.09, 67.55, 64.73, 39.54, 21.64, 18.10, 17.47, 15.96. The compound crystallizes with $MgCl_2$ present (confirmed by a qualitative Ag ion test).

X-ray Crystallographic Analysis. A suitable crystal of **5a** was grown from a saturated hexane solution at −30 °C. Crystal data may be found in Table 1. A preliminary investigation showed that the crystals were weakly diffracting. Data were collected on a Siemans P4 diffractometer with the XSCANS software package.[35] The Laue symmetry 2/*m* was determined by merging symmetry equivalent positions. A total of 6646 data were collected in the range of $\theta = 1.9-22.0°$ ($-1 \le h \le 11$, $-1 \le k \le 38$, $-12 \le l \le 12$). Three standard reflections monitored at the end of every 297 reflections collected showed no decay of the crystal. In the shell $38 \le 2\theta \le 44°$ only 3% of the reflections were found to be significant. The data processing, solution, and refinement were done using SHELXTL-PC programs.[36] The methyl carbons attached to Si(2) were found to have two different orientations with occupancies of 0.6 and 0.4. Similarly, the two methyl carbon atoms of the isopropyl group attached to C(27) were found to occupy two positions (occupancies 0.5 and 0.5). Common isotropic thermal parameters were refined for these disordered carbon atoms. An empirical absorption correction was applied to the data using the ψ scan data. No attempt was made to locate hydrogen atoms, were placed in calculated positions. The phenyl groups were constrained to be regular hexagons with C−C distances of 1.395 Å. In the final difference Fourier synthesis the electron density fluctuates in the range 0.385 to −0.346 e Å^{-3}.

(35) XSCANS: Siemans Analytical X-ray Instruments Inc., Madison WI, 1990.

(36) SHELXTL Version 5: Siemans Analytical X-ray Instruments Inc., Madison WI, 1994.

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Supporting Information Available: Text describing X-ray procedures, tables of final crystallographic atomic coordinates, equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, complete bond lengths and angles, and X-ray parameters, and an ORTEP diagram for **5a** (12 pages). Ordering information is given on any current masthead page.

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