Successive Insertion of Alkynes into a Tantalum−Alkynyl Bond: Implications for the Coordination Polymerization of Alkynes

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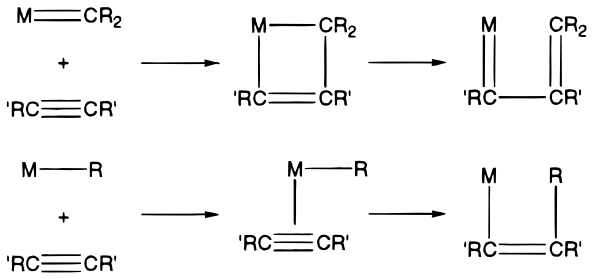
The reaction of 2,6-$[ArN(SiMe_3)CH_2]_2NC_5H_3$ (**1**, $BDPP(SiMe_3)_2$, Ar = 2,6-$^iPr_2C_6H_3$) with $TaCl_5$ yields the complex *mer*-$(BDPP)TaCl_3$ (**2**) and 2 equiv of $ClSiMe_3$. The reduction of compound **2** with excess Na/Hg in the presence of alkynes yields the pseudo 5-coordinate Ta(III) derivatives $(BDPP)Ta(\eta^2\text{-}RC{\equiv}CR')Cl$ (**3a**, R = R′ = Pr; **3b**, R = R′ = Et; **3c**, R = R′ = Ph; **3d**, R = Ph, R′ = H). An X-ray study of **3a** revealed a distorted square pyramidal geometry with the chloride occupying the apical position. Compound **3a** reacts with LiC≡CR to give the acetylide octyne derivatives $(BDPP)Ta(\eta^2\text{-}PrC{\equiv}CPr)(C{\equiv}CR)$ (**5a**, R = Ph; **5b**, R = Bu; **5c**, R = $SiMe_3$; **5d**, R = *o*-$Me_3SiC_6H_4$). Compound **5a** reacts with phenylacetylene to give the metallacyclic derivative $(BDPP)Ta[(\eta^2\text{-}PhC{\equiv}C)PrC{=}CPrHC{=}CPh]$ (**6a**). An X-ray study of **6a** again revealed a square pyramidal geometry with the alkenyl carbon occupying the apical position. Similarly, compounds **5b**,**c** react with HC≡CBu and HC≡$CSiMe_3$ to give the metallacycles $(BDPP)Ta[(\eta^2\text{-}BuC{\equiv}C)PrC{=}CPrHC{=}CBu]$ (**6b**) and $(BDPP)Ta[(\eta^2\text{-}Me_3SiC{\equiv}C)PrC{=}CPrHC{=}CSiMe_3]$ (**6b**), respectively. Compound **5b** reacts with HC≡CPh to give $(BDPP)Ta[(\eta^2\text{-}BuC{\equiv}C)PrC{=}CPrHC{=}CPh]$ (**7b**) only, establishing that the starting acetylide is retained in the final product.

Introduction

The polymerization of alkynes is catalyzed by certain group 5 metal complexes;[1−3] however, the active species are often ill-defined. Two mechanistic pathways have been proposed for this transformation: the 2 + 2 cycloaddition between an alkyne and a carbene which affords a vinyl-substituted carbene upon ring-opening;[4] the coordination insertion of an alkyne into a metal−carbon bond to give a propagating alkenyl species (Scheme 1).[5]

Scheme 1



Relevant to the latter mechanism, formally d^2 metal alkyl complexes are known to insert alkynes; however, the alkenyl complexes are typically reluctant to engage in further insertions. For example, the d^2 η^2-alkyne complex $Tp^*NbCl(CH_2CH_3)(\eta^2\text{-}PhC{\equiv}CCH_2CH_3)$ (Tp^* = hydrotris(3,5-dimethyl-pyrazolyl)borate) readily inserts the coordinated alkyne $PhC{\equiv}CCH_2CH_3$ but stops short of inserting additional alkyne.[6] Precursor complexes of the type $L_nTa(\eta^2\text{-}RC{\equiv}CR)X$ (**A**, X = alkyl, hydride, or halide),[7] where the metal is formally in the +3 oxidation state, are ideally suited for studying the latter mechanism. The choice of ancillary ligand system (L_n) for complexes of type **A** is critical since metallacyclopentadiene compounds can result from the coupling of alkynes, impeding the coordination insertion process. For instance, η^2-alkyne complexes are obtained with bis(cyclopentadienyl) templates (e.g., $Cp_2Ta(\eta^2\text{-}RC{\equiv}CR)X$)[8−10] and mono(pentamethylcyclopentadienyl) ligation (e.g.,

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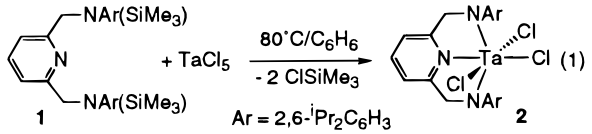
$Cp^*Ta(\eta^2\text{-}RC{\equiv}CR)X_2$),[11−13] while less coordinatively saturating alkoxide ligands yield metallacycles (e.g., $(DIPP)_3Ta(C_4Et_4)$, DIPP = 2,6-diisopropylphenoxide).[14]

Herein we describe the synthesis and alkyne insertion chemistry of η^2-alkyne complexes of tantalum bearing a pyridine diamide ligand, including an unusual double insertion of alkyne into a tantalum alkynyl bond. We have previously[15] shown that the pyridine diamide ligand imparts metallocene-like structural and electronic features on group 4 complexes while providing a variable steric environment about the metal. Some of this work has appeared in a preliminary form.[16]

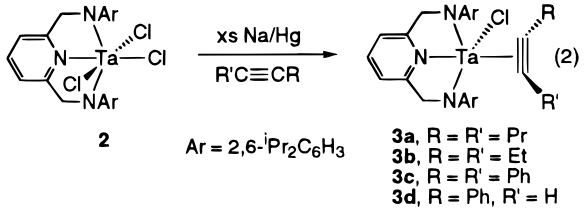
Results and Discussion

We have reported[17] the synthesis of the silylated pyridine diamine ligand 2,6-$[ArN(SiMe_3)CH_2]_2NC_5H_3$ (**1**, BDPP{$SiMe_3$}$_2$, Ar = 2,6-$^i Pr_2C_6H_3$). Compound **1** reacts cleanly with $TaCl_5$ at 80 °C in benzene to give 2 equiv of $ClSiMe_3$ (confirmed by ^{1}H NMR spectroscopy) and the yellow trichloride complex *mer*-(BDPP)$TaCl_3$ (**2**) in 84% yield (eq 1).



Compound **2** is contaminated with small amounts of unreacted $TaCl_5$; however, this impurity can be removed by dissolving the crude reaction solids in THF, followed by filtration. The proton NMR spectrum of compound **2** displays a sharp singlet at 5.84 ppm for the ligand methylene protons (NCH_2), confirming the meridional coordination of the ligand. The isopropyl methyl groups of the arene are diastereotopic, which is likely the result of restricted rotation about the N−C_{ipso} bond.

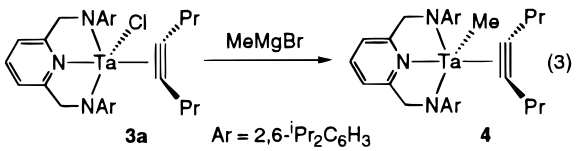
The reduction of compound **2** with excess Na/Hg amalgam in the presence of excess alkyne affords the pseudo 5-coordinate Ta(III) η^2-alkyne derivatives (BDPP)Ta(η^2-RC≡CR′)Cl (**3a**, R = R′ = Pr; **3b**, R = R′ = Et; **3c**, R = R′ = Ph; **3d**, R = Ph, R′ = H) in 51−82% yield (eq 2).



The ^{1}H NMR spectra of compounds **3a**−**d** display very similar features for the BDPP ligand; in particular, the methylene protons (NCH_2) appear as an AB quartet centered at about 5.1 ppm indicating that there is asymmetry about the N_3-plane of the ligand. In addition, the spectra show two isopropyl methine resonances and four isopropyl methyl resonances, which is consistent with the aforementioned asymmetry coupled with restricted arene rotation. A single low-field acetylenic carbon resonance is observed in the $^{13}C\{^1H\}$ NMR spectra of complexes **3a**−**c**, suggesting that the alkyne acts as a 4-electron donor.[18] Compound **3d** which bears a terminal alkyne (η^2-HC≡CPh) necessarily displays two low-field acetylenic resonances. Given the induced asymmetry of the BDPP ligand and since both ends of the coordinated alkynes in compound **3a**−**c** are spectroscopically equivalent, a rapid rotation of the alkynes on the NMR time scale is advanced. Compounds **3a**−**d** are surprisingly inert to excess amalgam which permits the use of excess amalgam. Furthermore, we see no evidence of metallacycle formation even under forcing conditions (excess alkyne 110 °C); hence, an excess of alkyne can be used in the synthesis. The coordinated alkynes do not exchange with free alkyne; for example, no reaction occurs between compound **3a** and 50 equiv of phenylacetylene at 80 °C.

The solid-state structure of **3a** was determined by X-ray crystallography (Table 1). The molecular structure of complex **3a** can be found in Figure 1, and relevant bond distances and angles are in Table 2. Overall the molecular structure is best described as a distorted square pyramid with the chloride (Cl(1)) occupying the apical position. The 4-octyne unit is located trans to the pyridine of the BDPP ligand and is rotated by about 50° with respect to the Cl(1)−Ta(1)−N(2) plane (Figure 1, bottom). The bond distances in the Ta−alkyne moiety are comparable to other mononuclear Ta(III) alkyne complexes reported.[12−14,19] Each amide is sp^2-hybridized as evidenced by the sum of the angles about each nitrogen (N(1) = 359.5° and N(3) = 359.9°). The rigid coordination of the ligand and enforced location of the aryl isopropyl groups creates a "pocket" opposite the pyridine and necessarily protects the metal above and below the N_3-plane.

To explore the insertion chemistry of $L_nTa(\eta^2\text{-}RC{\equiv}CR)R'$ (R′ = alkyl) type complexes, (BDPP)Ta(η^2-PrC≡CPr)Me (**4**) was prepared from **3a** and MeMgBr (eq 3).



The proton NMR spectrum of compound **4** displays a Ta−CH_3 resonance at 0.44 ppm while the carbon spectrum shows a resonance at 39.04 ppm. The coordinated 4-octyne in complex **4** does not insert into the Ta−Me bond at elevated temperatures (110 °C) even in the presence of PMe_3.

The reaction of compound **4** with an excess of phenylacetylene in toluene at 110 °C affords methane (confirmed by ^{1}H NMR spectroscopy) and the spectroscopi-

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Table 1. Crystal Data and Experimental Details for Compounds 3a and 6a

	3a	6a
empirical formula	$C_{39}H_{65}ClN_3Ta$	$C_{58}H_{73}N_3Ta$
fw	729.36	993.14
temp (°C)	23	20
wavelength (Å)	0.710 73	0.710 73
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
unit cell dimens	a = 9.936(2) Å b = 11.558(1) Å c = 17.689(2) Å α = 74.997(6)° β = 87.424(10)° γ = 75.372(9)°	a = 13.530(2) Å b = 18.389(2) Å c = 21.604(3) Å β = 102.98(1)°
V (Å^3)	1898.0(5)	5238(1)
Z	2	4
D_{calcd} (g cm^{-3})	1.386	1.259
F(000) electrons	820	2060
reflcns collcd	6078	18018
indepdt reflctns	5179 [R(int) = 0.0284]	5624 [R(int) = 0.0902]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	5179/90/408	5575/3/500
goodness-of-fit (GooF)[a]	1.037	1.230
final R indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0401, w$R2$ = 0.0946	$R1$ = 0.0794, w$R2$ = 0.1458
R indices (all data)[a]	$R1$ = 0.0519, w$R2$ = 0.1011	$R1$ = 0.1099, w$R2$ = 0.1593

[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).

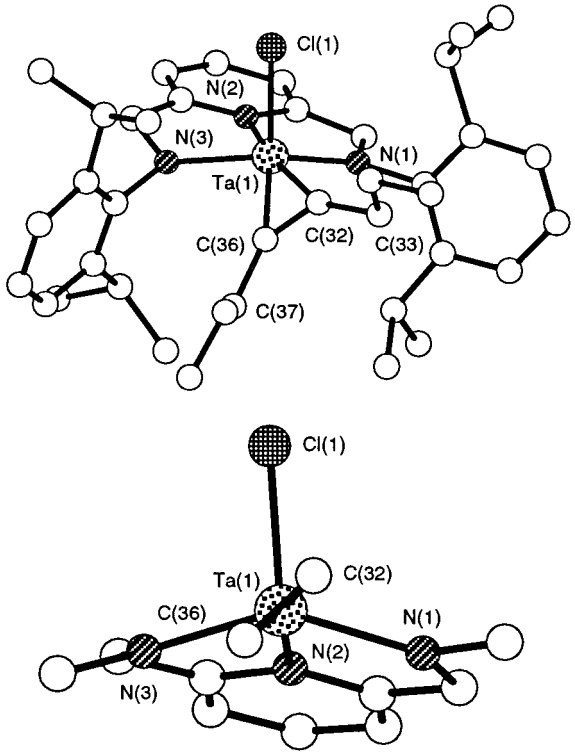


Figure 1. Top: Chem 3D representation of compound **3a**. Bottom: Chem 3D representation of the core of compound **3a** showing the orientation of the octyne unit. (The 2,6-diisopropylphenyl groups have been removed for clarity.)

cally and structurally characterized metallacycle **6a** in quantitative yield by ^{1}H NMR spectroscopy (eq 4).

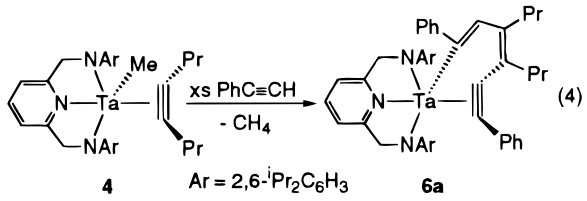


Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 3a

Bond Distances			
Ta(1)−N(1)	2.053(6)	Ta(1)−N(2)	2.255(6)
Ta(1)−N(3)	2.033(6)	Ta(1)−Cl(1)	2.361(2)
Ta(1)−C(32)	2.062(7)	Ta(1)−C(36)	2.085(7)
C(32)−C(36)	1.287(11)	Acet[a]−Ta	1.97
Bond Angles			
N(3)−Ta(1)−N(1)	137.2(2)	N(1)−Ta(1)−N(2)	71.4(2)
N(3)−Ta(1)−N(2)	71.9(2)	N(1)−Ta(1)−Cl(1)	106.6(2)
N(2)−Ta(1)−Cl(1)	93.7(2)	N(3)−Ta(1)−Cl(1)	96.9(2)
C(36)−C(32)−C(33)	132.6(8)	C(32)−C(36)−C(37)	137.2(8)

[a] Acet = midpoint of C(32)−C(36).

Compound **6a** is characterized by two low-field acetylenic resonances in the carbon NMR spectrum. In addition, the proton NMR spectrum displays resonances for two inequivalent propyl groups and two different phenyl moieties. The proton and carbon NMR resonances for the BDPP ligand indicate overall C_s symmetry in solution.

The solid-state structure of **6a** was determined by X-ray crystallography (Table 1). The molecular structure of complex **6a** can be found in Figure 2, and relevant bond distances and angles are in Table 3. The molecular structure of compound **6a** is very similar to **3a**; for example, the alkenyl carbon (C(6)) occupies the apical position of a distorted square pyramid (Cl(1) occupies the apical position in **3a**), while the acetylenic group (C(1)−C(2)) resides in the basal plane (the octyne unit resides in this position in compound **3a**). In comparison to complex **3a**, the acetylenic unit in compound **6a** is only rotated about 12° relative to the C(6)−Ta−N(16) plane which is likely a result of the restraints of the metallacycle. Alternating short and long bonds are observed in the metallacyclic unit (C(6) through to C(1)), consistent with the coupling of the alkynes and the acetylide.

Compound **6a** appears to result from the insertion of coordinated octyne into a Ta−CCPh bond, followed by a 2,1-insertion of phenylacetylene into the newly formed alkenyl unit. The 2,1-insertion of phenyl acetylene

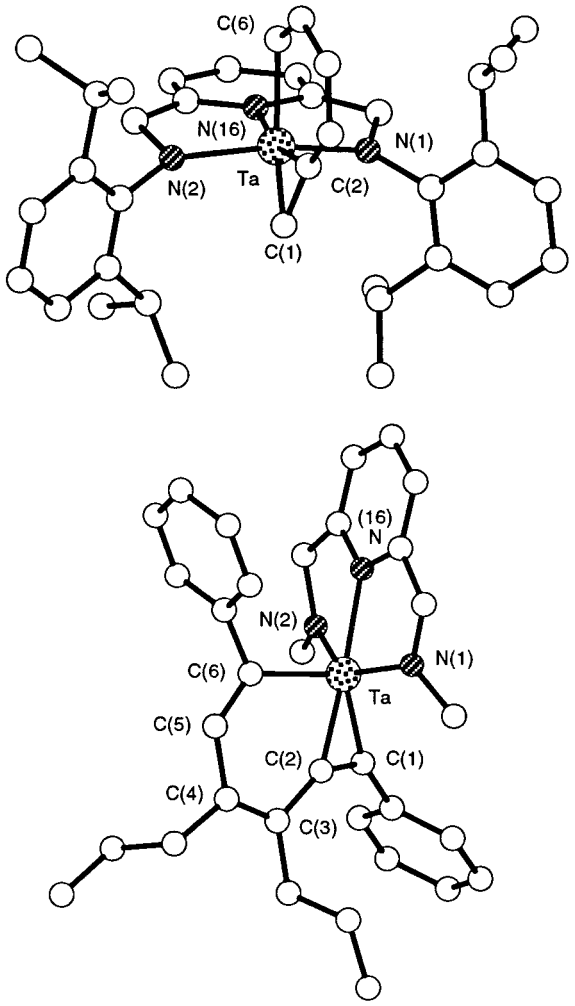
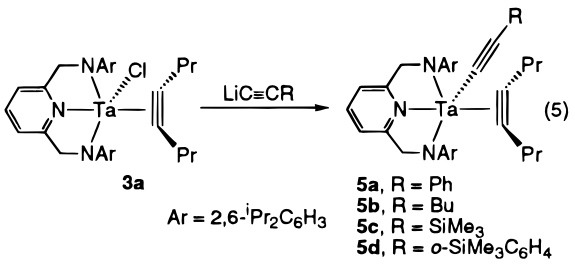


Figure 2. Top: Chem 3D representation of compound **6a** showing the orientation of the pyridine diamide ligand relative to the metallacycle. (The metallacycle substituents have been removed for clarity.) Bottom: Chem 3D representation of compound **6a** showing the substituents on the metallacycle. (The 2,6-diisopropylphenyl groups have been removed for clarity.)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 6a

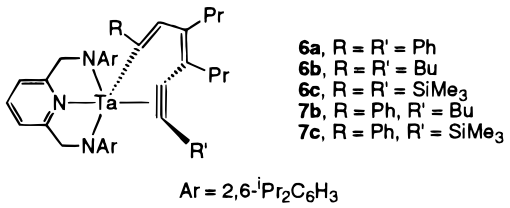
	Bond Distances		
Ta−N(1)	2.006(11)	Ta−N(2)	2.005(10)
Ta−N(16)	2.225(6)	Ta−C(1)	2.075(14)
Ta−C(2)	2.030(12)	Ta−C(6)	2.19(2)
C(1)−C(2)	1.30(2)	C(2)−C(3)	1.45(2)
C(3)−C(4)	1.33(2)	C(4)−C(5)	1.51(2)
C(5)−C(6)	1.37(2)		
	Bond Angles		
N(1)−Ta−N(2)	137.9(2)	N(1)−Ta−N(16)	71.4(4)
N(2)−Ta−N(16)	72.6(4)	N(1)−Ta−C(6)	102.8(5)
N(2)−Ta−C(6)	100.2(5)	N(16)−Ta−C(6)	93.0(4)
Ta−C(6)−C(5)	127.2(10)	C(6)−C(5)−C(4)	129.9(13)
C(5)−C(4)−C(3)	122.1(13)	C(4)−C(3)−C(2)	116.4(12)
C(3)−C(2)−C(1)	140.0(13)		

likely minimizes the interaction between the phenyl group and the propyl chains of the octyne unit. To demonstrate that an acetylide octyne complex is the intermediate in this reaction, a series of such compounds were prepared. Compound **3a** reacts cleanly with LiC≡CR in ether at −78 °C to give the acetylide derivatives **5a**−**d** (eq 5).



The ^{1}H NMR spectra of compounds **5a**−**d** display an AB quartet at 5.08−5.12 ppm for the ligand methylene protons (NCH_2) again indicating asymmetry about the N_3-plane of the ligand. The low-field acetylenic carbon resonances observed in the $^{13}C\{^1H\}$ NMR spectra of complexes **5a**−**d** are consistent with the octyne acting as a 4-electron donor.[18]

As expected, the reaction of the phenylacetylide derivative **5a** with phenylacetylene in toluene at 110 °C affords the metallacycle **6a** in quantitative yield by



proton NMR spectroscopy. Compound **5a** does not react with internal alkynes (4-octyne, 3-hexyne) at 110 °C. In a similar way, the reaction of the acetylides **5b** and **5c** with 1-hexyne and (trimethylsilyl)acetylene gives the new metallacyclic products **6b**,**c**, respectively.

The proton NMR resonances for the BDPP ligand in complex **6b** are very similar to those observed for the phenyl-substituted derivative **6a**; hence, the compounds are likely isostructural. In contrast, the ^{1}H NMR spectrum of compound **6c** is quite different, displaying resonances for a single species with C_1-symmetry (**6a,b** display C_s-symmetry in solution). For example, two AB quartets are observed for the ligand methylene protons (NCH_2), along with four isopropyl methine and eight isopropyl methyl resonances. Regioisomers of the metallacycle, that is, those arising from both a 1,2- and a 2,1-insertion of (trimethylsilyl)acetylene, can be discounted since there are only two silylmethyl resonances in the proton and carbon spectra of compound **6c**. Assuming compound **6c** has the same basic features as complexes **6a**,**b**, we conclude that the two trimethylsilyl groups in the metallacycle cause the aryl groups of the ligand to twist relative to one another about the N−C_{ipso} bond, thus avoiding interaction with these bulky groups. The primary interaction that may be responsible for this observation is the one between the trimethylsilyl group bound to the η^2-alkyne unit and the isopropyl groups adjacent to it (vide infra). No change in the spectral features of compound **6c** are observed to 80 °C.

Compounds **5b**,**c** react with excess phenylacetylene to give only the mixed metallacycles **7b**,**c**, respectively. The absence of compound **6a** suggests that the starting acetylide unit is retained in the final product. Compound **7c** which bears one trimethylsilyl group on the η^2-alkyne unit also displays C_1-symmetry in solution.

As noted above, the interaction of this group with the isopropyl groups of the arene may cause the aryl groups to distort.

In an attempt to discourage the coordination of the alkyne unit once the metallacycle is formed, possibly leading to the polymerization of alkynes, the bulky (*o*-(trimethylsilyl)phenyl)acetylide derivative **5d** was reacted with HC≡CPh, HC≡CBu, and HC≡CSiMe$_3$ in toluene at 110 °C. Surprisingly, compound **5d** does not react with these alkynes over several days. It is not clear why this particular acetylide derivative is reluctant to engage in what appears to be a general reaction. We have attempted to trap the proposed intermediate alkenyl species "(BDPP)Ta(PrC=CPrC≡CPh)" formed via the insertion of the octyne into the phenylacetylide bond; however, no reaction occurs between compound **5a** and a variety of Lewis bases (PMe$_3$, py, NEt$_3$) at 110 °C in toluene. Alternatively, the initial reaction between compound **5a** and HC≡CPh could involve the formation of the metallacyclopentadiene acetylide intermediate "(BDPP)Ta(PhC=CHPrC=CPr)(C≡CPh)", followed by coupling of the metallacycle and the acetylide. This seems unlikely since we see no evidence of metallacyclopentadiene formation between compound **3a** and HC≡CPh at elevated temperatures (110 °C).

Conclusion

The pyridine diamide ligand BDPP affords a steric and electronic mimic of a metallocene environment for alkyne derivatives of tantalum. In contrast to complexes of the type Cp$_2$Ta(η^2-RC≡CR)R′ (R = alkyl, aryl; R′ = alkyl), the acetylide derivatives (BDPP)Ta(η^2-PrC≡CPr)(C≡CR) (R = Ph, Bu, SiMe$_3$) readily engage in alkyne insertion chemistry. What appears to prevent this system from undergoing multiple insertions of alkyne is the relatively strong interaction between the alkyne unit of the metallacycle and tantalum. We are currently examining complexes of the type (BDPP)Ta(η^2-PrC≡CPr)X (X = vinyl and −C≡N) in the hope that these moieties will be reluctant to participate in bonding with tantalum once incorporated into the proposed alkenyl intermediate.

Experimental Details

General Details. All experiments were performed under a dry dinitrogen 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. Tantalum(V) chloride was purchased from Alfa and used as received. Diphenylacetylene, phenylacetylene, 3-hexyne, 1-hexyne, 4-octyne, and MeMgBr were purchased from Aldrich and used as received. The (*o*-(trimethylsilyl)phenyl)-acetylene was prepared using a previously reported synthesis.[20] The acetylides LiC≡CR (R = Ph, Bu, SiMe$_3$, *o*-Me$_3$SiC$_6$H$_4$) were prepared from BuLi and the appropriate acetylene in hexanes at 25 °C. Unless otherwise specified, proton (300 MHz) and carbon (75.46 MHz) NMR spectra were recorded in C$_6$D$_6$ at approximately 22 °C on a Varian Gemini-300 or 300-XL spectrometer. The proton chemical shifts were referenced to internal C$_6$D$_5$*H* (δ = 7.15 ppm), and the carbon resonances, to C$_6$D$_6$ (δ = 128.0 ppm). Elemental analyses were performed using sealed tin cups on a Fisons Instruments model 1108 elemental analyzer by Mr. Peter Borda of this department or by Oneida Research Services Inc., Whitesboro, NY. BDPP = [2,6-(ArNCH$_2$)$_2$NC$_5$H$_3$]$^{2-}$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

***mer*-(BDPP)TaCl$_3$ (2).** Solid TaCl$_5$ (2.670 g, 7.454 mmol) was added in small portions to a benzene (150 mL) solution of BDPP(SiMe$_3$)$_2$[17] (4.087 g, 6.768 mmol) at 23 °C. The turbid solution immediately turned bright yellow and was heated to 80 °C for 12 h. The volatile compounds were removed under vacuum, and the resulting solid was dissolved in THF (50 mL). The solution was filtered through Celite and the solvent removed in *vacuo*. The resulting solid was washed with hexanes (3 × 50 mL) to yield a bright yellow crystalline solid **2** (4.204 g, 5.658 mmol, 84%). ^{1}H NMR: δ 7.14 (m, 6H, Ar), 6.84 (t, 1H, py), 6.38 (d, 2H, py), 5.84 (s, 4H, NC*H*$_2$), 3.80 (sept, 4H, C*H*Me$_2$), 1.52 (d, 12H, CH*Me*$_2$), 1.12 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR: δ 161.64, 148.84, 146.56, 139.66, 125.35, 122.28, 117.51, 71.78, 28.89, 27.57, 23.64. Anal. Calcd for C$_{31}$H$_{41}$N$_3$TaCl$_3$: C, 50.11; H, 5.56; N, 5.66. Found: C, 50.25; H, 5.68; N, 5.11.

(BDPP)Ta(η^2-PrC≡CPr)Cl (3a). A toluene (30 mL) solution of compound **2** (0.500 g, 0.673 mmol) and 4-octyne (0.297 g, 2.70 mmol) was added to an excess of Na/Hg amalgam (0.460 g of Na, 20.0 mmol; 46.0 g of Hg). The mixture was stirred for 12 h. The solution was decanted from the amalgam and filtered through Celite. The solvent was removed in *vacuo* to yield an orange-brown solid. The solid was dissolved in a minimum amount of diethyl ether and cooled to −30 °C for 12 h. Yellow crystalline **3a** was isolated by filtration and dried under vacuum (0.401 g, 0.513 mmol, 75%). ^{1}H NMR: δ 7.19 (t, 2H, Ar), 7.13 (d, 4H, Ar), 6.85 (t, 1H, py), 6.39 (d, 2H, py), 5.12 (AB quartet, $^2J_{HH}$ = 20.1 Hz, 4H, NC*H*$_2$), 3.79 (sept, 2H, C*H*Me$_2$), 3.15 (sept, 2H, C*H*Me$_2$), 2.51 (m, 4H, ≡CC*H*$_2$), 1.46 (d, 6H, CH*Me*$_2$), 1.34 (m, 4H, C*H*$_2$CH$_3$), 1.32 (d, 6H, CH*Me*$_2$), 1.24 (d, 6H, CH*Me*$_2$), 1.01 (d, 6H, CH*Me*$_2$), 0.84 (t, 6H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR: δ 237.01 (*C*≡*C*), 160.77, 154.41, 145.19, 142.96, 138.41, 125.49, 124.32, 123.57, 116.99, 70.95, 40.02, 28.60, 27.95, 26.66, 25.76, 24.61, 23.80, 21.94, 15.45. Anal. Calcd for C$_{39}$H$_{55}$N$_3$TaCl: C, 59.88; H, 7.09; N, 5.37. Found: C, 59.62; H, 7.19; N, 5.16.

(BDPP)Ta(η^2-EtC≡CEt)Cl (3b). The preparation of compound **3b** is identical to that for **3a**. Compound **2** (0.500 g, 0.673 mmol), 3-hexyne (0.200 g, 2.43 mmol), and excess Na/Hg amalgam (0.186 g Na, 8.09 mmol; 18.6 g Hg) gave yellow crystalline **3b** (0.417 g, 0.553 mmol, 82%). ^{1}H NMR: δ 7.19, (t, 2H, Ar), 7.11 (d, 4H, Ar), 6.84 (t, 1H, py), 6.39 (d, 2H, py), 5.11 (AB quartet, $^2J_{HH}$ = 20.1 Hz, 4H, NC*H*$_2$), 3.79 (sept, 2H, C*H*Me$_2$), 3.13 (sept, 2H, C*H*Me$_2$), 2.59 (q, 4H, ≡CC*H*$_2$), 1.46 (d, 6H, CH*Me*$_2$), 1.32 (d, 6H, CH*Me*$_2$), 1.21 (d, 6H, CH*Me*$_2$), 1.02 (d, 6H, CH*Me*$_2$), 0.94 (t, 6H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR: δ 237.81 (*C*≡*C*), 160.76, 154.34, 145.17, 142.88, 138.41, 125.57, 124.35, 123.59, 117.01, 70.94, 30.56, 28.53, 27.94, 26.69, 25.76, 24.61, 23.77, 13.03. Anal. Calcd for C$_{37}$H$_{51}$N$_3$TaCl: C, 58.92; H, 6.82; N, 5.57. Found: C, 58.97; H, 6.70; N, 5.38.

(BDPP)Ta(η^2-PhC≡CPh)Cl (3c). The preparation of compound **3c** is identical to that for **3a**. Compound **2** (1.001 g, 1.346 mmol), diphenylacetylene (0.288 g, 1.62 mmol), and excess Na/Hg amalgam (0.619 g Na, 26.9 mmol; 61.9 g Hg) gave yellow crystalline **3c** (0.567 g, 0.667 mmol, 51%). ^{1}H NMR: δ 7.15−6.95 (m, 17H, Ar and Ph), 6.48 (d, 2H, py), 5.14 (AB quartet, $^2J_{HH}$ = 19.5 Hz, 4H, NC*H*$_2$), 4.02 (sept, 2H, C*H*Me$_2$), 3.30 (sept, 2H, C*H*Me$_2$), 1.30 (d, 6H, CH*Me*$_2$), 1.08 (d, 12H, CH*Me*$_2$), 1.04 (d, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR: δ 228.20 (*C*≡*C*), 159.94, 152.52, 147.23, 145.25, 144.13, 138.67, 126.96, 126.17, 124.55, 124.03, 117.37, 70.90, 28.85, 28.59, 27.56, 25.93, 24.33, 23.95. Anal. Calcd for C$_{45}$H$_{51}$N$_3$TaCl: C, 63.56; H, 6.05; N, 4.94. Found: C, 63.21; H, 6.07; N, 4.42.

(BDPP)Ta(η^2-PhC≡CH)Cl (3d). The preparation of compound **3d** is identical to that for **3a**. Compound **2** (0.250 g, 0.336 mmol), phenylacetylene (0.103 g, 1.01 mmol), and excess

(20) Masuda, T.; Hamano, T.; Tsuchihara, K.; Higashimura, T. *Macromolecules* **1990**, *23*, 1374.

Na/Hg amalgam (0.230 g of Na, 10.0 mmol; 23.0 g of Hg) gave ivory crystalline **3d** (0.207 g, 0.267 mmol, 79%). ^{1}H NMR: δ 11.91 (s, 1H, C≡C*H*) 7.20−6.90 (m, Ar and Ph), 6.83 (t, 1H, py), 6.36 (d, 2H, py), 5.08 (AB quartet, $^2J_{HH}$ = 20.3 Hz, 4H, NCH_2), 3.82 (sept, 2H, C*H*Me$_2$), 3.43 (sept, 2H, C*H*Me$_2$), 1.31 (d, 6H, CH*Me*$_2$), 1.26 (d, 6H, CH*Me*$_2$), 1.20 (d, 6H, CH*Me*$_2$), 1.08 (d, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR: δ 236.45 (Ph*C*≡C), 225.81(C≡*C*H), 160.65, 152.78, 146.77, 145.38, 142.25, 138.68, 126.86, 125.94, 124.35, 123.69, 117.30, 70.60, 28.54, 27.96, 26.47, 26.27, 24.70, 23.99.

(BDPP)Ta(η^2-PrC≡CPr)Me (4). To a diethyl ether (25 mL) solution of compound **3a** (0.600 g, 0.767 mmol) was added 1.2 equiv of MeMgBr (0.38 mL, 2.4 M, 0.91 mmol) at −78 °C. The yellow solution was warmed to 25 °C and stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite to give a bright yellow solution. The solvent was removed in vacuo, the solid esd dissolved in a minimum amount of diethyl ether, and the solution was cooled to −30 °C for 12 h. Yellow crystalline **4** was isolated by filtration and dried under vacuum (0.531 g, 0.697 mmol, 91%). ^{1}H NMR: δ 7.22−7.10 (m, 6H, Ar), 6.88 (t, 1H, py), 6.45 (d, 2H, py), 5.05 (AB quartet, $^2J_{HH}$ = 20.5 Hz, 4H, NCH_2), 3.60 (sept, 2H, C*H*Me$_2$), 3.15 (sept, 2H, C*H*Me$_2$), 2.46 (m, 4H, ≡CCH_2), 1.42 (d, 6H, CH*Me*$_2$), 1.34 (m, 4H, CH_2CH$_3$), 1.33 (d, 6H, CH*Me*$_2$), 1.21 (d, 6H, CH*Me*$_2$), 1.05 (d, 6H, CH*Me*$_2$), 0.86 (t, 6H, CH$_2$CH_3), 0.44 (s, 3H, Me). ^{13}C-{^{1}H} NMR: δ 237.45 (*C*≡*C*), 161.93, 155.12, 144.61, 143.12, 138.05, 124.84, 124.02, 123.61, 116.98, 70.69, 39.06 (Ta−*C*H$_3$), 37.94, 28.78, 27.75, 26.49, 25.80, 24.56, 23.84, 22.10, 16.63. Anal. Calcd for $C_{40}H_{58}N_3Ta$: C, 63.06; H, 7.67; N, 5.52. Found: C, 63.02; H, 7.79; N, 6.38.

(BDPP)Ta(η^2-PrC≡CPr)(C≡CPh) (5a). To a diethyl ether (25 mL) solution of compound **3a** (0.500 g, 0.634 mmol) was added 1.1 equiv of PhC≡CLi (0.076 g, 0.703 mmol) at −78 °C. The yellow solution was warmed to 25 °C and stirred for 12 h. The solvent was removed in *vacuo*. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite to give a bright yellow solution. The solvent was removed in vacuo, the solid was dissolved in a minimum amount of pentane, and the solution was cooled to −30 °C for 12 h. Yellow crystalline **5a** was isolated by filtration and dried under vacuum (0.406 g, 0.479 mmol, 76%). ^{1}H NMR: δ 7.59 (m, 2H, Ph), 7.22−7.10 (m, 7H, Ar and Ph), 7.01 (m, 2H, Ph), 6.80 (t, 1H, py), 6.38 (d, 2H, py), 5.08 (AB quartet, $^2J_{HH}$ = 20.2 Hz, 4H, NCH_2), 4.10 (sept, 2H, C*H*Me$_2$), 3.39 (sept, 2H, C*H*Me$_2$), 2.81 (m, 4H, ≡CCH_2), 1.53 (d, 6H, CH*Me*$_2$), 1.39 (d, 6H, CH*Me*$_2$), 1.36 (d, 6H, CH*Me*$_2$), 1.22 (m, 4H, CH_2CH$_3$), 1.10 (d, 6H, CH*Me*$_2$), 0.87 (t, 6H, CH$_2$CH_3). ^{13}C{^{1}H} NMR δ 233.64 (Pr*C*≡*C*Pr), 161.41, 153.22, 149.40, 145.21, 143.08, 138.16, 130.97, 127.12, 126.48, 126.23, 125.33, 124.32, 123.35, 117.05, 70.99, 40.96, 28.86, 27.84, 27.09, 25.93, 24.94, 24.10, 21.95, 15.52.

(BDPP)Ta(η^2-PrC≡CPr)(C≡CBu) (5b). The preparation of compound **5b** is identical to that of complex **5a**. Complex **3a** (0.100 g, 0.128 mmol) and LiC≡CBu (0.012 g, 0.128 mmol) yielded orange crystalline **5b** (0.077 g, 0.093 mmol, 73%). ^{1}H NMR: δ 7.24 (t, 2H, Ar), 7.14 (d, 4H, Ar), 6.85 (t, 1H, py), 6.41 (d, 2H, py), 5.09 (AB quartet, $^2J_{HH}$ = 20.1 Hz, 4H, NCH_2), 4.05 (sept, 2H, C*H*Me$_2$), 3.32 (sept, 2H, C*H*Me$_2$), 2.67 (m, 4H, CH_2CH$_2$Me), 2.22 (t, 2H, TaC≡CCH_2), 1.52 (d, 6H, CH*Me*$_2$), 1.44 (d, 6H, CH*Me*$_2$), 1.40 (m, 8H, CH_2 of octyne and butylacetylide), 1.31 (d, 6H, CH*Me*$_2$), 1.08 (d, 6H, CH*Me*$_2$), 0.88 (t, 6H, CH$_2$CH$_2$*Me*), 0.87 (t, 3H, CH$_2$CH$_2$CH$_2$*Me*). ^{13}C{^{1}H} NMR: δ 235.46 (Pr*C*≡*C*Pr), 161.46, 153.90, 145.11, 143.04, 139.10, 137.98, 125.50, 125.08, 124.16, 123.33, 116.88, 70.78, 40.50, 32.09, 28.70, 27.64, 27.02, 25.79, 24.88, 23.95, 22.19, 22.04, 21.36, 15.53, 13.91.

(BDPP)Ta(η^2-PrC≡CPr)(C≡CSiMe$_3$) (5c). The preparation of compound **5c** is identical to that of **5a**. Complex **3a** (0.100 g, 0.128 mmol) and LiC≡CSiMe$_3$ (0.013 g, 0.128 mmol) yielded yellow crystalline **5c** (0.102 g, 0.121 mmol, 95%). ^{1}H NMR: δ 7.19 (t, 2H, Ar), 7.15 (d, 4H, Ar), 6.77 (t, 1H, py), 6.34 (d, 2H, py), 5.00 (AB quartet, $^2J_{HH}$ = 20.2 Hz, 4H, NCH_2), 4.01 (sept, 2H, C*H*Me$_2$), 3.35 (sept, 2H, C*H*Me$_2$), 2.77 (m, 4H, CH_2CH$_2$Me), 1.51 (d, 6H, CH*Me*$_2$), 1.43 (d, 6H, CH*Me*$_2$), 1.32 (d, 6H, CH*Me*$_2$), 1.19 (m, 4H, CH$_2$CH_2Me), 1.06 (d, 6H, CH*Me*$_2$), 0.85 (t, 6H, CH$_2$CH$_2$*Me*), 0.26 (s, 9H, SiMe$_3$). ^{13}C {^{1}H} NMR: δ 232.68 (Pr*C*≡*C*Pr), 169.14, 161.22, 153.05, 145.02, 143.08, 138.15, 130.89, 125.32, 124.33, 123.31, 117.04, 70.91, 40.89, 28.85, 27.52, 27.10, 25.88, 25.07, 24.11, 21.86, 15.47, 1.21.

(BDPP)Ta(η^2-PrC≡CPr)(C≡C-*o*-Me$_3$SiC$_6$H$_4$) (5d). The preparation of complex **5d** is identical to that of complex **5a**. Complex **3a** (0.100 g, 0.128 mmol) and LiC≡C-*o*-Me$_3$SiC$_6$H$_4$ (0.023 g, 0.128 mmol) yielded orange crystalline **5d** (0.087 g, 0.095 mmol, 74%). ^{1}H NMR: δ 7.83 (d, 1H, Ph), 7.40 (d, 1H, Ph), 7.20−6.90 (m, 9H, Ar, py and Ph), 6.54 (d, 2H, py), 5.12 (AB quartet, $^2J_{HH}$ = 20.4 Hz, 4H, NCH_2), 3.99 (sept, 2H, C*H*Me$_2$), 3.43 (sept, 2H, C*H*Me$_2$), 2.87 (m, 4H, CH_2CH$_2$Me), 1.43 (d, 6H, CH*Me*$_2$), 1.37 (d, 6H, CH*Me*$_2$), 1.35 (m, 4H, CH$_2$CH_2Me), 1.30 (d, 6H, CH*Me*$_2$), 1.10 (d, 6H, CH*Me*$_2$), 0.91 (t, 6H, CH$_2$CH$_2$*Me*), 0.21 (s, 9H, SiMe$_3$). ^{13}C {^{1}H} NMR: δ 233.304 (Pr*C*≡*C*Pr), 161.67, 153.07, 152.80, 145.27, 142.98, 138.25, 133.99, 133.54, 132.40, 129.22, 128.88, 126.26, 125.30, 124.29, 123.29, 117.20, 70.89, 40.83, 28.85, 27.78, 26.95, 25.96, 24.77, 24.06, 21.95, 15.50, −1.00. Anal. Calcd for $C_{50}H_{68}N_3SiTa$: C, 65.27; H, 7.45; N, 4.57. Found: C, 65.48; H, 7.59; N, 4.80.

(BDPP)Ta[(η^2-PhC≡C)PrC=CPrHC=CPh] (6a). To a toluene solution (5 mL) of compound **5a** (0.100 g, 0.118 mmol) in a glass pressure vessel was added 1.5 equiv of phenylacetylene (0.018 g, 0.177 mmol) at 25 °C. The yellow solution was stirred at 110 °C for 12 h. The solvent was removed in vacuo. The resulting orange solid was dissolved in a minimum amount of diethyl ether, and the solution was cooled to −30 °C for 12 h. Orange crystalline **6a** was isolated by filtration and dried under vacuum (0.108 g, 0.114 mmol, 97%). ^{1}H NMR: δ 7.19−7.10 (m, 6H, Ar), 7.05 (s, 1H, PhC=C*H*), 7.04−6.98 (m, 4H, Ph), 6.90 (t, 2H, Ph), 6.82 (tt, 1H, Ph), 6.76 (t, 1H, py), 6.74 (tt, 1H, Ph), 6.25 (d, 2H, py), 5.60 (dd, 2H, Ph), 4.87 (AB quartet, $^2J_{HH}$ = 20.1 Hz, 4H, NCH_2), 4.10 (sept, 2H, C*H*Me$_2$), 3.36 (sept, 2H, C*H*Me$_2$), 2.24 (m, 4H, ≡CH_2), 1.62 (m, 2H, ≡CH_2), 1.43 (d, 6H, CH*Me*$_2$), 1.35 (d, 6H, CH*Me*$_2$), 1.22 (m, 2H, CH_2CH$_3$), 1.08 (d, 6H, CH*Me*$_2$), 1.01 (d, 6H, CH*Me*$_2$), 0.93 (t, 3H, CH$_2$CH_3), 0.51 (t, 3H, CH$_2$CH_3). ^{13}C{^{1}H} NMR: δ 220.26 (PhC≡*C*H), 189.90 (Ph*C*≡CH), 160.83, 158.63, 154.09, 151.86, 147.39, 145.14, 144.72, 142.08, 137.95, 128.89, 127.16, 126.73, 125.69, 125.47, 124.08, 123.98, 123.87, 123.34, 116.85, 71.21, 37.31, 34.30, 29.03, 27.95, 27.83, 25.92, 24.88, 24.58, 23.52, 23.30, 15.24, 14.68. Anal. Calcd for $C_{55}H_{66}N_3Ta$: C, 69.53; H, 7.00; N, 4.42. Found: C, 69.95; H, 7.41; N, 4.71.

(BDPP)Ta[(η^2-BuC≡C)PrC=CPrHC=CBu] (6b). The preparation of compound **6b** is identical to that of compound **6a**. Complex **5b** (0.100 g, 0.098 mmol) and HC≡CBu (0.010 g, 0.122 mmol) yielded red crystalline **6b** (0.086 g, 0.078 mmol, 80%). ^{1}H NMR: δ 7.17−7.05 (m, 6H, Ar), 6.91 (t, 1H, py), 6.85 (s, 1H, BuC=C*H*), 6.46 (d, 2H, py), 4.98 (AB quartet, $^2J_{HH}$ = 21.0 Hz, NCH_2), 3.66 (sept, 2H, C*H*Me$_2$), 3.59 (sept, 2H, C*H*Me$_2$), 2.77 (m, 2H, CH_2CH$_2$Me), 2.48 (m, 2H, CH_2CH$_2$Me), 2.34 (t, 2H, CH_2CH$_2$CH$_2$Me), 2.23 (br m, 2H, CH_2CH$_2$CH$_2$Me), 1.63 (m, 4H, CH$_2$CH_2CH$_2$Me), 1.42 (d, 6H, CH*Me*$_2$), 1.33 (d, 6H, CH*Me*$_2$), 1.26 (d, 6H, CH*Me*$_2$), 1.12 (d, 6H, CH*Me*$_2$), 1.30 (buried, 8H, CH_2 Pr and Bu), 1.00, 0.86, 0.82, and 0.71 (t, 3H each, CH$_2$*Me* Pr and Bu). ^{13}C{^{1}H} NMR: δ 237.52, 236.28, 195.53, 162.11, 153.35, 145.00, 144.20, 141.34, 140.95, 138.11, 137.01, 128.09, 124.27, 123.25, 116.19, 71.52, 43.49, 39.59, 37.17, 35.27, 34.96, 31.15, 28.84, 27.29, 26.99, 25.99, 25.33, 24.50, 24.42, 23.76, 23.65, 21.99, 15.23, 14.81, 14.58, 14.10.

(BDPP)Ta[(η^2-Me$_3$SiC≡C)PrC=CPrHC=CSiMe$_3$] (6c). The synthesis of compound **6c** is identical to that of **6a**. Complex **5c** (0.100 g, 0.096 mmol) and HC≡CSiMe$_3$ (0.015 g, 0.153 mmol) yielded red crystalline **6c** (0.113 g, 0.088 mmol, 92%). ^{1}H NMR: δ 7.10−6.90 (m, 7H, Ar and py), 6.54 (d, 1H,

py), 6.49 (d, 1H, py), 5.17 (AB quartet, $^2J_{HH}$ = 19.4 Hz, 2H, NCH_2), 4.93 (AB quartet, $^2J_{HH}$ = 20.4 Hz, 2H, NCH_2), 4.08 (sept, 1H, CHMe$_2$), 3.58 (sept, 1H, CHMe$_2$), 3.08 (sept, 1H, CHMe$_2$), 2.96 (m, 1H, CH_2CH$_2$Me), 2.90 (s, 1H, CH≡CSiMe$_3$), 2.67 (m, 2H, CHMe$_2$ and CH_2CH$_2$Me), 2.36 (m, 1H, CH_2CH$_2$-Me), 2.24 (m, 1H, CH_2CH$_2$Me), 1.84 (m, 1H, CH$_2$CH_2Me), 1.64 (m, 1H, CH$_2$CH_2Me), 1.57 (d, 3H, CHMe_2), 1.51 (d, 3H, CHMe_2), 1.27 (d, 3H, CHMe_2), 1.26 (d, 3H, CHMe_2), 1.20 (m, 2H, CH$_2$CH_2Me), 1.10 (d, 3H, CHMe_2), 1.08 (d, 3H, CHMe_2), 1.08 (buried, 3H, CH$_2$CH$_2$*Me*), 1.06 (d, 3H, CHMe_2), 0.92 (d, 3H, CHMe_2), 0.74 (t, 3H, CH$_2$CH$_2$*Me*), 0.28 (s, 9H, SiMe$_3$), −0.19 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR: δ 233.53, 190.05, 169.56, 167.86, 163.49, 162.93, 155.43, 154.54, 145.76, 144.21, 143.31, 142.58, 138.57, 132.39, 124.51, 123.93, 123.84, 123.51, 123.37, 122.32, 117.11, 116.88, 68.81, 68.59, 55.34, 33.06, 29.98, 29.03, 27.48, 27.36, 27.28, 26.10, 25.84, 25.12, 24.86, 24.25, 24.17, 24.00, 22.57, 14.83, 14.69, 3.95, −0.51.

(BDPP)Ta[(η^2-BuC≡C)PrC=CPrHC=CPh] (7b). The synthesis of compound **7b** is identical to that of **6a**. Complex **5b** (0.100 g, 0.098 mmol) and HC≡CPh (0.015 g, 0.147 mmol) yielded red crystalline **7b** (0.076 g, 0.068 mmol, 69%). ^{1}H NMR: δ 7.30−7.10 and 6.90−6.70 (m, 12H, Ar, Ph and py), 6.14 (d, 2H, Ph), 5.38 (AB quartet, $^2J_{HH}$ = 19.9 Hz, 4H, NCH_2), 4.16 (sept, 2H, CHMe$_2$), 3.39 (m, 2H, CH_2CH$_2$CH$_2$Me), 3.11 (s, 1H, PhC=CH), 3.05 (sept, 2H, CHMe$_2$), 2.30 (m, 2H, CH_2-CH$_2$Me), 1.65 (m, 4H, CH_2 Pr or Bu), 1.60 (m, 4H, CH_2 Pr or Bu), 1.49 (d, 6H, CHMe_2), 1.43 (d, 6H, CHMe_2), 1.35 (d, 6H, CHMe_2), 1.22 (m, 5H, CH_2 and CH_3, Pr or Bu), 1.02 (d, 6H, CHMe_2), 0.97 (t, 3H, CH_3 Pr or Bu), 0.81 (t, 3H, CH_3 Pr or Bu). ^{13}C{^{1}H} NMR: δ 221.17, 204.45, 163.86, 162.56, 156.19, 149.68, 148.58, 148.10, 143.55, 138.81, 127.03, 126.20, 125.16, 123.46, 123.27, 117.30, 70.91, 48.59, 34.79, 28.77, 28.65, 28.25, 27.55, 24.31, 23.44, 23.13, 22.84, 15.88, 15.40.

(BDPP)Ta[(η^2-Me$_3$SiC≡C)PrC=CPrHC=CPh] (7c). The synthesis of compound **7c** is identical to that of **6a**. Complex **5c** (0.100 g, 0.096 mmol) and HC≡CPh (0.015 g, 0.147 mmol) yielded red crystalline **7c** (0.097 g, 0.076 mmol, 79%). ^{1}H NMR: δ 7.50−6.50 (m, 10H, Ar, Ph and py), 6.37 (d, 1H, py), 6.35 (d, 1H, py), 6.21 (d, 2H, Ph), 5.01 (AB quartet, $^2J_{HH}$ = 20.1 Hz, 2H, NCH_2), 4.97 (AB quartet, $^2J_{HH}$ = 20.1 Hz, 2H, NCH_2), 4.10 (sept, 1H, CHMe$_2$), 3.77 (br m, 4H, CHMe$_2$ and PhC=CH), 2.55 (m, 1H, CH_2CH$_2$Me), 2.41 (m, 3H, CH_2CH$_2$-Me), 1.78 (m, 4H, CH$_2$CH_2Me), 1.60 (d, 3H, CHMe_2), 1.53 (d, 3H, CHMe_2), 1.38 (d, 3H, CHMe_2), 1.31 (d, 3H, CHMe_2), 1.24 (d, 3H, CHMe_2), 1.00−0.84 (m, 15H, CH$_2$CH$_2$*Me* and CHMe_2), −0.29 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR: δ 240.72, 234.10, 192.94, 161.07, 160.43, 156.69, 156.16, 154.01, 153.35, 153.02, 146.04, 144.64, 144.21, 144.05, 143.59, 140.09, 139.37, 138.96, 138.00, 136.14, 131.14, 127.11, 126.80, 126.72, 126.14, 125.86, 125.43, 124.84, 124.46, 124.64, 124.11, 123.90, 123.88, 116.70, 116.65, 71.76, 71.44, 38.95, 31.13, 30.33, 29.93, 28.05, 27.20, 26.94, 26.45, 26.29, 25.77, 25.39, 24.60, 24.23, 24.14, 22.86, 22.78, 15.34, 15.10, 0.54.

X-ray Crystallographic Analysis of 3a. A suitable crystal of **3a** (dimension 0.45 × 0.23 × 0.20 mm) was grown from a saturated ether solution at −30 °C. Data were collected on a Siemens P4 diffractometer with the XSCANS software package.[21] The cell constants were obtained by centering 25 reflections (18.0 = 2θ = 24.7°). The Laue symmetry $\bar{1}$ was determined by merging symmetry equivalent positions. The data were collected in the range of θ = 1.9−23° (−1 ≤ h ≤ 10, −11 ≤ k ≤ 12, −19 ≤ l ≤ 19) in ω mode at variable scan speeds (2−20 deg/min). Four standard reflections monitored at the end of every 297 reflections collected showed no decay of the crystal. The data processing, solution, and refinement were done using SHELXTL-PC programs.[22] The final refinements were performed using SHELXL-93 software programs.[23] An empirical absorption correction was applied to the data using the routine "XEMP" on the basis of the ψ scans of 11 reflections with 2θ ranging from 8.5 to 25.9° (μ = 2.995 mm^{-1}). The methyl carbon atoms attached to C(29) were found to be disordered. Three orientation (0.33/0.33/0.33) of C(30) and C(31) were located in the final difference Fourier methods. Isotropic thermal parameters were refined for these disordered carbon atoms. Anisotropic thermal parameters were refined for all non-hydrogen atoms. No attempt was made to locate the hydrogen atoms; however, they were placed in calculated positions. The C−C distances in the isopropyl groups were restrained to be equal using the option SADI. In the final difference Fourier synthesis the electron density fluctuates in the range 0.788 to −0.677 e Å^{-3}.

X-ray Crystallographic Analysis of 6a. A suitable crystal of **6a** (dimension 0.10 × 0.1 × 0.1 mm) was grown from a saturated ether solution at −30 °C. Data were collected on a Siemens Smart system CCD diffractometer. The data were collected in the range of θ = 1.47−21° (−17 ≤ h ≤ 17, −11 ≤ k ≤ 23, −28 ≤ l ≤ 27). Unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. The systematic absences in the diffraction data and the determined unit-cell parameters were uniquely consistent for the reported space group. A trial application of a semiempirical absorption correction based on redundant data at varying effective azimuthal angles yielded T_{max}/T_{min} at unity and was ignored. A molecule of cocrystallized *n*-hexane solvent was located at the inversion center. All C−C distances in the solvent molecule were constrained to be equal. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. The structure was solved by direct methods, completed by subsequent Fourier syntheses, and refined with full-matrix least-squares methods. All scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library.[24] In the final difference Fourier synthesis the electron density fluctuates in the range 0.667 to −0.634 e Å^{-3}.

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Supporting Information Available: Tables listing final crystallographic atomic coordinates, equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, and complete bond lengths and angles and ORTEP's for **3a** and **6a** (19 pages). Ordering information is given on any current masthead page.

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