ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

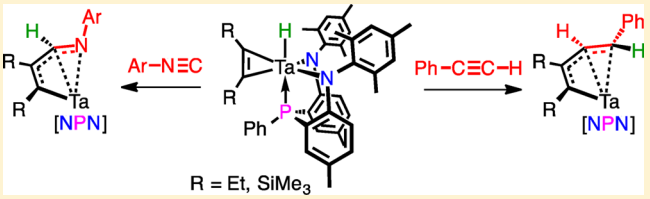
Carbon−Carbon Bond Forming Reactions with Tantalum Diamidophosphine Complexes That Incorporate Alkyne Ligands

Kyle D. J. Parker and Michael D. Fryzuk*

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1

Supporting Information

ABSTRACT: The incorporation of *o*-phenylene-linked diamidophosphine ligands onto the readily available alkyne complexes Ta(alkyne)Cl_3(DME) (where alkyne = hex-3-yne or 1,2-bis(trimethylsilylacetylene); DME = 1,2-dimethoxyethane) results in the formation of a versatile set of starting materials of the general formula [^{Ph}NPN*]Ta(alkyne)Cl (where [^{Ph}NPN*] = PhP(2-(*N*-mesityl)-5-Me-C_6H_3)$_2$). Upon reaction with $KBEt_3H$, the synthesis of the corresponding hydride complexes [^{Ph}NPN*]Ta(alkyne)H can be achieved; these complexes feature extremely downfield (δ ∼21 ppm) doublet resonances ($^2J_{HP}$ = ∼35 Hz) in the respective ^{1}H NMR spectra that are assigned to the newly formed Ta−H moieties. Subsequent reaction of these Ta hydrides with 2,6-dimethylphenylisocyanide and phenylacetylene results in the insertion of these species into the Ta−H bond and the formation of the corresponding iminoformyl and phenylvinyl complexes, respectively. While the former intermediate cannot be detected, the latter was characterized by NMR spectroscopy. Both of these processes result in the further transformation to generate C−C coupled products by a reductive elimination sequence with the coordinated alkyne; in the case of the iminoformyl, an azadiene results, whereas with the phenylvinyl derivative a butadienyl fragment is generated. Single-crystal X-ray diffraction and a suite of NMR spectroscopic techniques were used to characterize these species. A discussion of the bonding of the products in the context of the process by which they form is presented. The rate of formation of the butadienyl moiety from the phenylvinyl intermediate results in the activation parameters of $\Delta H^{\ddagger}$ = 22.2 ± 0.3 kcal/mol and $\Delta S^{\ddagger}$ = −8.7 ± 0.2 cal/(mol)(K).



INTRODUCTION

Alkynes are well known in the organometallic literature as being versatile ligands for transition metal complexes. They offer a number of different bonding modes and electron counts[1−6] and are important participants in a variety of carbon−carbon bond forming reactions. Historically, late metal (Pt, Pd, Ni, Co) alkyne complexes dominated in terms of their use as reagents in organic synthesis, mediating a variety of transformations ranging from cyclotrimerization of alkynes to the preparation of pyridines and cyclopentadienones from alkynes and isonitriles, olefins, or carbon monoxide.[7−9] With respect to early transition metals, a number of group 5 (Nb and Ta) metal alkyne complexes have also been shown to participate in cyclotrimerization reactions,[10−17] as well as mediate coupling reactions between alkynes and a variety of small-molecule substrates.[16,18,19] Related work by Rosenthal and co-workers has focused on a series of group 4 (Zr and Hf) alkyne complexes that react with ketones, olefins, carbodiimides, and other cumulenes, resulting in metallacycle ring expansion via the formation of new C−C bonds.[20−25]

The formation of C−C bonds is an area of particular utility and interest for synthetic chemists. Aside from the seminal advances in the realm of Pd-catalyzed cross-coupling, complexes of group 4 and 5 metals are well known to catalyze the coupling of amines and unsaturated hydrocarbons to afford new C−N and C−C bonds, via hydroamination and hydroaminoalkylation, respectively.[26−32] In addition, there are a variety of examples of Nb and Ta complexes serving as hydride or alkyl transfer agents for ketones,[33−38] imines,[33,37−41] and alkyne substrates.[42−46] These systems also provide further examples of metal-mediated C−C bond formation, as the resulting iminoacyl or vinyl moieties are also known to couple with coordinated alkyne units, resulting in the formation of more complex metallacyclic products featuring 1,3-butadienyl[44] or 1-aza-1,3-butadienyl[34,35,47] (AD) organic fragments.

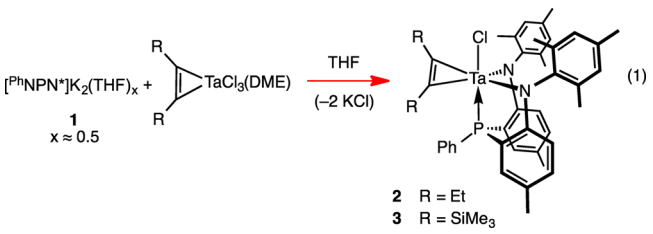
In this work, we report the synthesis of a series of tantalum alkyne complexes that incorporate an *ortho*-phenylene-bridged diamidophosphine ancillary ligand. We also present the synthesis of monohydride derivatives of these complexes and their reactivity with 2,6-dimethylphenyl isocyanide and phenylacetylene.

RESULTS AND DISCUSSION

Synthesis of [^{Ph}NPN*]Ta Complexes Featuring an Activated Alkyne Unit. Tantalum complexes of [^{Ph}NPN*] (where [^{Ph}NPN*] = PhP(2-(*N*-mesityl)-5-Me-C_6H_3)$_2$) can be prepared via the salt metathesis reaction between [^{Ph}NPN*]-$K_2(THF)_x$ (**1**) and Ta(alkyne)Cl_3(DME) (where DME = 1,2-dimethoxyethane), as shown in eq 1.[^{Ph}NPN*]Ta(hex-3-

Received: July 30, 2014
Published: October 13, 2014

   dx.doi.org/10.1021/om500775c | *Organometallics* 2014, 33, 6122−6131



yne)Cl, **2**, is obtained as a dark yellow solid in good yield. In C_6D_6, the ^{1}H NMR spectrum of **2** is consistent with a C_s symmetric complex; there are resonances due to four distinct aryl methyl groups, along with the expected aryl resonances. At room temperature, the methyl and methylene groups of the hexyne unit appear as two broad singlets at δ 2.95 (methylene) and 1.03 (methyl), which integrate to the expected four and six protons, respectively; the broadness of these resonances suggests that the position of the hexyne unit is fluxional, likely as a result of slow rotation of the hexyne unit about the Ta–hexyne centroid. In the variable-temperature ^{1}H NMR experiment, the methyl and methylene protons of the hexyne unit resolve into two pairs of triplets and quartets ($^3J_{HH}$ = 7 Hz in both cases) at 243 K and coalesce into a single triplet and quartet at 358 K. From these data, the $\Delta G^{\ddagger}_{rot}$ was determined to be 16.4 ± 0.3 kcal/mol; the full details of these VT-NMR experiments can be found in the Supporting Information.

The $^{13}C\{^1H\}$ NMR spectrum features all the expected resonances for the [^{Ph}NPN*] ligand; however, the carbon resonances of the hexyne unit are more complicated. Resonances for the methyl and methylene carbons appear as very weak singlets at δ 14.1 and 29.2, respectively; no resonances attributable to the metal-bound carbons are observable in a room-temperature $^{13}C\{^1H\}$ spectrum, likely due to signal broadening of these weak quaternary carbon resonances caused by the rotation of the hexyne unit. Indeed, the $^{13}C\{^1H\}$ NMR spectrum collected at 243 K contains two weak downfield resonances at δ 182.1 and 200.6 assigned to the metal-bound hexyne carbons. In addition, these carbon atoms can be detected indirectly using a ^{1}H–^{13}C HMBC NMR experiment, via their long-range coupling to the hexyne methyl and methylene protons; in C_6D_6 at room temperature, this method correlates these metal-bound hexyne carbons to a single ^{13}C NMR resonance at δ 204.4.

Slow evaporation of a concentrated toluene/pentane solution of **2** afforded bright yellow single crystals suitable for X-ray crystallography; the ORTEP representation of the solid-state molecular structure of **2** is shown in Figure 1. The [^{Ph}NPN*] ligand coordinates facially to Ta, resulting in significantly distorted trigonal bipyramidal geometry about the metal center; the quasi-apical positions are occupied by the Cl and P atoms, and the equatorial plane consists of N01, N02, and the centroid of the C41–C42 bond. The P01–Ta01–N01, P01–Ta01–N02, and P01–Ta01–Cl01 bond angles are significantly more acute than the expected value of 90° or 180°, respectively, due to structural demands of the arene bridge of the ligand.[48] The angle between the plane defined by P01, Ta01, and Cl01 (the σ_v symmetry plane of the molecule) and the plane defined by C41, C42, and Ta01 is 2.8°; this results in inequivalent alkyne carbon atoms in the solid state, which agrees with what is observed in the $^{13}C\{^1H\}$ NMR spectrum at 243 K.

The bond lengths between the Ta center and the hexyne unit are 2.075(3) and 2.126(3) Å, which are slightly shorter than a typical Ta–C single bond (2.20–2.25 Å),[49,50] but similar to the

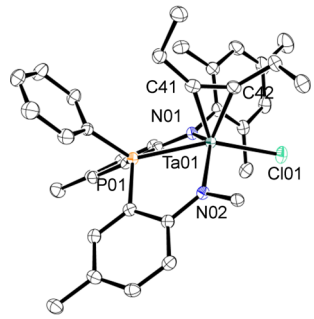
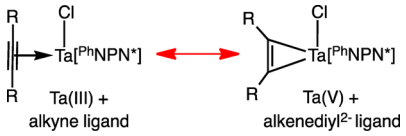


Figure 1. ORTEP drawing of the solid-state molecular structure of **2** (ellipsoids at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta01–N01 2.060(2), Ta01–N02 2.055(2), Ta01–P01 2.5728(6), Ta01–Cl01 2.4112(6), Ta01–C41 2.126(3), Ta01–C42 2.075(3), C41–C42 1.295(4), N01–Ta01–N02 131.46(8), P01–Ta01–Cl01 153.63(2), N01–Ta01–P01 74.41(6), N02–Ta01–P01 73.98(6), N01–Ta01–Cl01 94.98(6), N02–Ta01–Cl01 97.34(6).

distances observed in the starting trichloride complex[19] (2.046(9) and 2.102(7) Å); the Ta01–C41 bond is slightly longer than the Ta01–C42 bond, likely due to steric crowding from the phosphine Ph group. The C41–C42 bond length is 1.295(4) Å, which is noticeably shorter than the analogous bond length found in the starting trichloride[19] (1.39(1) Å) and more indicative of a bond order intermediate between 2 and 3.

Alkyne ligands are well known to be variable electron donors, in part mediated by the electrophilicity of the metal center.[4−6] Consequently, the interaction between the metal center and the 3-hexyne unit in complex **2** can be viewed as a dative bond between Ta(III) and a neutral (two- or four-electron-donating) alkyne ligand. Alternatively, the interaction can be viewed as a metallacyclopropene-type structure, with the donation of four electrons via two formal covalent bonds between Ta(V) and an "alkenediyl" dianion. Resonance structures that depict these two extremes are depicted in Scheme 1.

Scheme 1



Despite these two possible formalisms, complex **2** and its various congeners will be referred to as metal–alkyne complexes; this nomenclature is chosen for simplicity and brevity, despite the fact that the spectroscopic data point toward a more metallacyclopropene-type structure.

[^{Ph}NPN*]Ta(BTA)Cl (**3**, where BTA is bis(trimethylsilylacetylene)) is prepared via the reaction of eq 1 and Ta(BTA)Cl_3(DME) and is isolated as a light orange powder in good yield. The ^{1}H NMR spectrum of **3** is similar to that of **2** with four aryl methyl resonances; the aryl region of the spectrum is consistent with C_s symmetry. Two distinct trimethylsilyl groups appear in the expected region (δ 0.16 and 0.08), suggesting that in solution the entire alkyne unit lies in the σ_v plane of symmetry. The metal-bound carbons of the alkyne unit are attributed to two singlets at δ 225.3 and 205.4 in the $^{13}C\{^1H\}$ NMR spectrum.

The ORTEP representation of the solid-state molecular structure of **3** is shown in Figure 2. As with **2**, the [^{Ph}NPN*]

dx.doi.org/10.1021/om500775c | Organometallics 2014, 33, 6122–6131

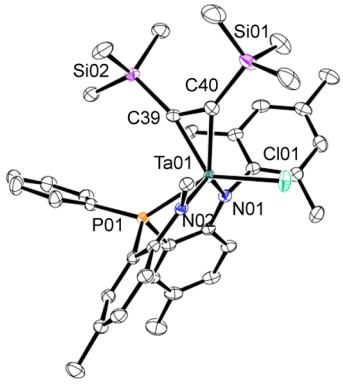
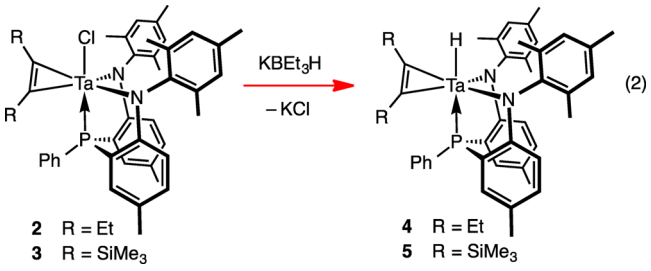


Figure 2. ORTEP drawing of the solid-state molecular structure of **3** (ellipsoids at 50% probability). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta01−N01 2.058(2), Ta01−N02 2.042(2), Ta01−P01 2.619(6), Ta01−Cl01 2.405(6), Ta01−C39 2.168(2), Ta01−C40 2.095(2), C39−C40 1.326(3), N01−Ta01−N02 132.86(8), P01−Ta01−Cl01 145.59(2), N01−Ta01−P01 73.62(6), N02−Ta01−P01 73.99(6), N01−Ta01−Cl01 91.96(6), N02−Ta01−Cl01 95.91(6).

ligand coordinates facially to Ta, resulting in significantly distorted trigonal bipyramidal geometry about the metal center; the apical positions are occupied by the Cl and P atoms, and the equatorial plane consists of N01, N02, and the centroid of the C39−C40 bond. Compounds **2** and **3** have similar solid-state structures; in general, they exhibit small but unremarkable differences with respect to bond lengths and angles. These structural similarities include the coordinated alkyne; the Ta01−C39, Ta01−C40, and C39−C40 bond lengths are comparable to those found in **2**. In addition, the plane defined by C39, C40, and Ta01 deviates from the P01−Ta01−Cl01 plane (the molecular plane of symmetry, σ_v) by only 5.2°. This is consistent with the observation of two distinct $SiMe_3$ groups in solution.

Synthesis of [^{Ph}NPN*]Ta Alkyne Monohydride Complexes. Both [^{Ph}NPN*]Ta(hex-3-yne)H (**4**) and [^{Ph}NPN*]-Ta(BTA)H (**5**) can be prepared from their corresponding chloride complexes via a salt metathesis reaction with freshly prepared $KBEt_3H$, as shown in eq 2.



The $^{13}C\{^1H\}$ NMR spectra of both **4** and **5** are similar to their chloride precursors (**2** and **3**); all of the [^{Ph}NPN*] resonances are present in their expected regions and are indicative of C_s symmetric complexes. In contrast to **2**, the quaternary alkyne carbons for **4** are directly observable in the expected region (at δ 205 and 184); the quaternary alkyne carbons for **5** also appear as expected at δ 220 and 193.

A noteworthy feature of the ^1H NMR spectrum for both **4** and **5** is the extremely downfield chemical shift of the hydride ligand;[51−53] in both cases these doublet resonances appear at δ ~21 ppm and exhibit strong coupling ($^2J_{HP} \approx 35$ Hz) to the phosphorus-31 nucleus of the [^{Ph}NPN*] ligand, suggesting that in solution these hydrides are *trans* to the phosphine. This assertion is borne out by the solid-state structural data discussed below. The remainder of ^1H NMR spectra for complexes **4** and **5** is consistent with C_s symmetry in solution. As with **3**, the trimethylsilyl groups in **5** give rise to two distinct singlets, which indicates that the alkyne unit lies in the σ_v plane of symmetry (a hypothesis supported by the inequivalent metal-bound alkyne carbon atoms mentioned above). Whereas in the case of **2** the ethyl arms of the 3-hexyne unit displayed considerable fluxionality and consequently result in two broad singlets in the room-temperature ^1H NMR spectrum, in complex **4** these methyl and methylene protons give rise to two pairs of well-resolved triplets and quartets ($^3J_{HH} = 7$ Hz in both cases), respectively. This observation, along with the presence of two inequivalent alkyne quaternary carbons in the $^{13}C\{^1H\}$ spectrum, implies that the two ethyl arms are inequivalent in solution and that the hexyne unit lies along the σ_v plane of symmetry, similar to the examples discussed above.

The ORTEP representation of the solid-state molecular structure of **4** is shown in Figure 3. The structure of **4**

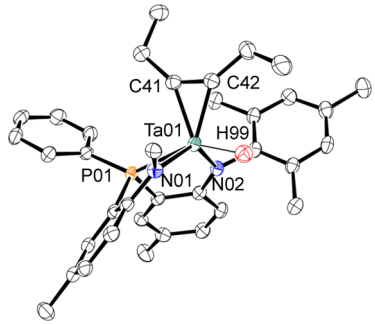


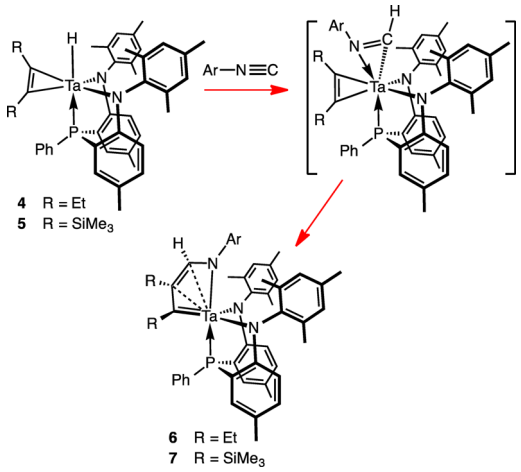
Figure 3. ORTEP drawing of the solid-state molecular structure of **4** (ellipsoids at 50% probability). All hydrogen atoms (except for H99, which was located from the difference map and refined isotropically) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta01−N01 2.041(2), Ta01−N02 2.037(2), Ta01−P01 2.647(1), Ta01−H99 1.82(3), Ta01−C41 2.109(3), Ta01−C42 2.084(3), C41−C42 1.300(5), N01−Ta01−N02 130.27(10), P01−Ta01−H99 148.8(11), N01−Ta01−P01 74.84(7), N02−Ta01−P01 73.52(7), N02−Ta01−H99 93.20(11), N01−Ta01−H99 94.60(11).

resembles that of **2**, with only small differences in bond angles and lengths. Again, the geometry at Ta is that of a significantly distorted trigonal bipyramid; the P atom of [^{Ph}NPN*] and the hydride ligand occupy the apical positions, with N01, N02, and the centroid of the C41−C42 bond constituting the equatorial plane. In the solid state the hexyne unit lies in the σ_v plane of symmetry, leading to two inequivalent ethyl arms, which is consistent with the solution NMR data. The bond lengths related to the coordinated hexyne unit (Ta01−C41, Ta01−C42, and C41−C42) are all very similar to those found in **2** and reflect an analogous metal−ligand interaction.

Reactions of 4 and 5 with 2,6-Dimethylphenyl Isocyanide. The addition of 1 equiv of 2,6-dimethylphenyl isocyanide to a toluene solution of **4** or **5** leads within 5 min to the full consumption of the starting hydride complex and the quantitative formation of a new species, **6** or **7** (Scheme 2). Upon workup, the ^1H NMR spectrum of **6** or **7** in C_6D_6 features aryl [^{Ph}NPN*] ligand resonances suggestive of a C_1 symmetric complex, in addition to a new singlet (**6** = δ 4.85; **7**

dx.doi.org/10.1021/om500775c | *Organometallics* 2014, 33, 6122−6131

Scheme 2



= δ 5.24) for a proton that a $^{13}C-^{1}H$ HSQC experiment indicates to be carbon-bound (**6** = δ 93.9; **7** = δ 107.6). As well, there are 10 distinct singlets attributable to aryl methyl groups (eight from the [^{Ph}NPN*] ligand and two from the isocyanide moiety) in the expected region (δ 2.3–1.6). An obvious structure consistent with this data is that of an iminoformyl complex generated from insertion of the isocyanide into the Ta–H bond (square brackets, Scheme 2).

However, an X-ray diffraction study instead revealed the formation of a five-membered tantallacyclic product. Bright red single crystals of **7** were obtained from a concentrated hexanes solution cooled to −30 °C, and the ORTEP representation (Figure 4) shows a structure in which the putative iminoformyl moiety has coupled with the coordinated alkyne to generate an 1-aza-1,3-butadiene ligand. Three molecules—representing both enantiomeric forms of **7**—are present in the unit cell, although for clarity only one is depicted.

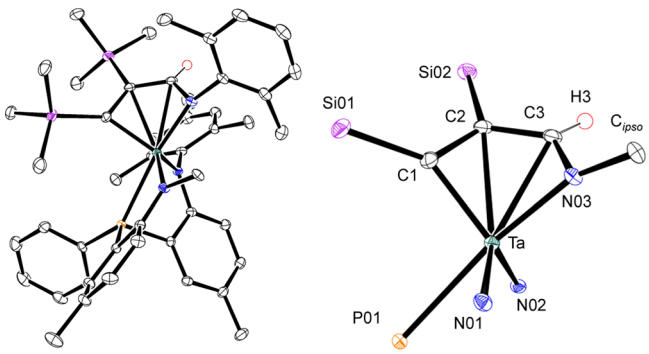
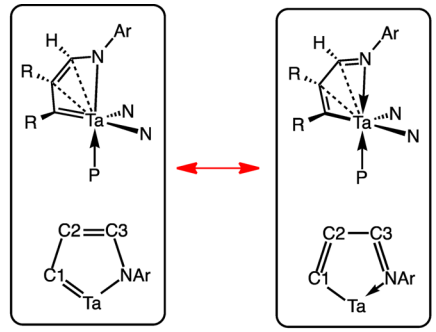


Figure 4. ORTEP diagram of the solid-state molecular structure of **7** (left) and truncated ORTEP diagram of the core of **7** (right) with ellipsoids drawn at 50% probability. All hydrogen atoms (except H3) and the silyl methyl groups at Si01 and Si02 have been omitted for clarity; H3 was located from the difference map and refined isotropically. Selected bond lengths (Å) and angles (deg): Ta–N03: 2.022(2), Ta–C3: 2.418(3), Ta–C2: 2.445(3), Ta–C1: 1.976(3), N03–C3: 1.412(4), C3–C2: 1.401(4), C2 –C1: 1.463(4), Ta–P01: 2.595(1) Ta–N01: 2.077(2), Ta–N02: 2.103(3), Ta–N03–C3: 87.7(2), Ta–C1–C2: 89.3(2), N03–Ta–C1: 89.59(10), N01–Ta–N02: 124.46(9), P01–Ta–N03: 168.97, N03–C3–C2: 121.9(3), H3–C3–C2: 118.4(20), C3–C2–C1: 117.2(2), N03–C3–C2–C1 (dihedral): 1.4.

The near planarity (dihedral angle ≅1°) of the N03–C3–C2–C1 fragment is a defining feature of this structural motif. Also, the AD fragment is bent back toward the tantalum in a supine-type mode, which is well established for AD-type ligands coordinated to the early transition metal complexes.[54−56] Two possible resonance forms are shown in Scheme 3 for the AD

Scheme 3



metallacycle. The solid-state structural data are more consistent with the amido–alkylidene resonance structure: in particular, the short Ta–C1 bond length of 1.976(3) Å is indicative of a metal–carbene interaction. Furthermore, the Ta–N3 distance of 2.022(2) Å is similar to the Ta–amido bond lengths of the diamidophosphine [^{Ph}NPN*] ancillary ligand (cf. Ta–N01: 2.077(2), Ta–N02: 2.103(3) Å).

The $^{13}C\{^{1}H\}$ NMR spectra of **6** and **7** are typical of C_1 symmetric complexes featuring a 1-aza-1,3-butadiene moiety. The $^{13}C\{^{1}H\}$ NMR spectrum of **6** features two pairs of singlets that correspond to the inequivalent methylene and methyl carbons of the former hexyne moiety, whereas in the case of **7**, there are two distinct singlets that correspond to inequivalent trimethylsilyl groups. Resonances for the carbon atoms of the 1-aza-1,3-butadiene fragment are in excellent agreement with other similar complexes:[47] C1 (**6**: δ 232, **7**: δ 242), C2 (**6**: δ 111, **7**: δ 111), and C3 (**6**: δ 94, **7**: δ 107). The extremely downfield chemical shift for C1 is typical for a metal-bound alkylidene and is consistent with similar metal–AD bonding models.[47,54,55,57]

The synthesis of an 1-aza-1,3-butadienyl moiety via the reaction of an organic isocyanide and an early transition metal complex is not without precedent. There are numerous examples in the literature of isocyanide insertion into Ta–C bonds to produce an η^2-iminoacyl[33−38,47,58−60] functionality, and there are several examples of the coupling of these iminoacyl units with coordinated alkynes,[34,35,47] or indeed other iminoacyls,[58−65] to form 1-aza-1,3-butadiene or 1,4-diazabutadiene ligands, respectively.

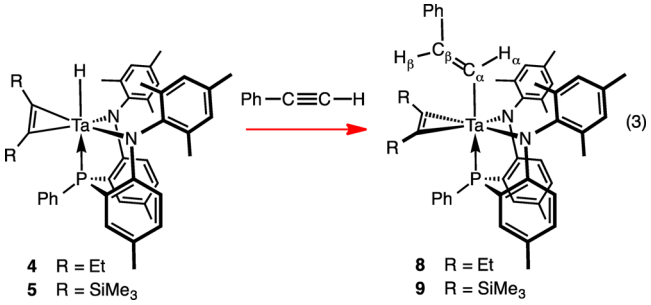
However, there are few examples of stable, well-characterized iminoformyl complexes[46] generated from isocyanide insertion into early metal–hydride bonds. The majority of reports feature products that are either incompletely characterized (usually due to rapid decomposition),[66−68] contain a μ-η^2:η^2 RN=CH unit bridging between two metal centers,[69−71] or have a strongly coordinated phosphine adduct at the iminoformyl C atom.[72,73] In this context, it appears that the highly electrophilic iminoformyl moiety strongly favors further reactivity, which frustrates isolation and characterization of a mononuclear, adduct-free example. Complexes **6** and **7** appear to be the first

dx.doi.org/10.1021/om500775c | *Organometallics* 2014, 33, 6122–6131

reported examples of a 1-aza-1,3-butadiene moiety generated from the coupling of an iminoformyl and a coordinated alkyne.

This type of C−C bond formation is not limited to the highly reactive iminoformyl fragment. As shown in the next section, a similar process also occurs with the more stable phenylvinyl fragment generated by addition of phenylacetylene.

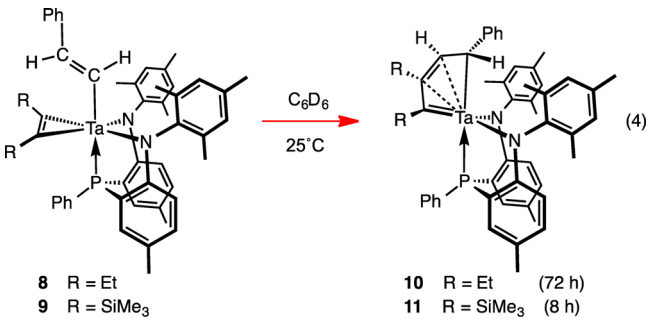
Reactions of 4 and 5 with Phenylacetylene. The addition of 1 equiv of phenylacetylene to a benzene solution of **4** at room temperature results in an immediate brown to dark red color change. After 5 min the starting Ta hydride complex is rapidly converted to complex **8** via 1,2-insertion of phenylacetylene into the Ta−H bond to generate a Ta



alkyne−phenylvinyl complex, as shown in eq 3.In C_6D_6, the ^{1}H NMR spectrum features two doublets, at δ 8.62 and 6.08, that correspond to the newly formed phenylvinylic protons; the large coupling constant shared by these protons ($^3J_{HH}$ = 18 Hz) is indicative of *trans*-vicinal, rather than geminal, stereochemistry, which is reflected in the depiction of the alkene moiety in eq 3.[46,72,73] This assignment is buttressed by the results of a ^{1}H−^{13}C HSQC experiment, which indicates that the phenylvinylic protons are located on separate carbon atoms. Synthesis of the isotopologue of **8** with PhCCD, and the subsequent absence of the ^{1}H resonance at δ 8.62, allows for the unambiguous identification of these phenylvinylic carbons: δ 204.3 (C_α), 142.1 (C_β). The methyl and methylene groups on the hexyne moiety appear as one quartet and one triplet (J_{HH} = 7.5 Hz) integrating to four and six protons, respectively, rather than the two pairs of triplets and quartets seen in complex **4**. These data indicate that the hexyne unit is oriented perpendicular to the σ_v plane of the molecule, in contrast to the coplanar orientation seen in complexes **2**−**5**. However, as the static geometry depicted in eq 3 would result in diastereotopic methylene protons, the NMR data also imply fast exchange of the two halves of the hexyne ligand, via rotation about the Ta−alkyne bond.

Complex **5** also reacts with phenylacetylene to generate **9**, a Ta alkyne−phenylvinyl complex similar to **8** (eq 3). The ^{1}H NMR spectrum of **9** in C_6D_6 contains two doublets at δ 8.92 and 5.83 ($^3J_{HH}$ = 18 Hz) that correspond well with the data for the phenylvinylic protons in **8**; the rest of the ^{1}H NMR spectrum of **9** agrees with the proposed C_s symmetric structure, including a single resonance for the two TMS groups, implying that the BTA moiety is arranged perpendicular to the σ_v plane. Further characterization of **9** is hampered by its thermal instability and rapid (~8 h) structural rearrangement to complex **11**, as will be discussed in more detail below.

Structural Rearrangement of Complexes 8 and 9. A benzene solution of **8** left to sit at room temperature cleanly converts to a second complex, **10**, over the course of approximately 3 days (eq 4). The ^{1}H and ^{13}C{^{1}H} NMR



spectra of **10** are extremely complicated, and full structural elucidation was possible only after obtaining a solid-state molecular structure from a single-crystal X-ray analysis; ORTEP representations for complex **10** are shown in Figure 5.

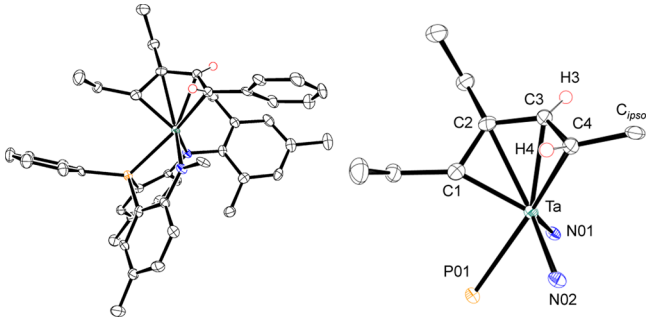


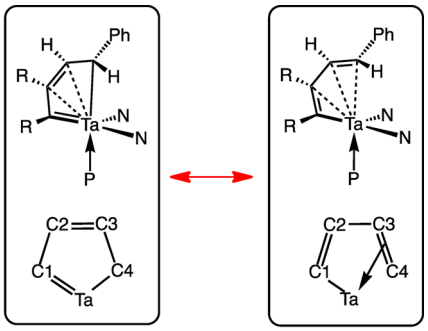
Figure 5. ORTEP diagram of the solid-state molecular structure of **10** (left) and truncated ORTEP diagram of the core of **10** (right) with ellipsoids drawn at 50% probability.

All hydrogen atoms (except H3 and H4) and the mesityl group at N02 (except for C_{ipso}) have been omitted for clarity; H3 and H4 were located from the difference map and refined isotropically. Selected bond lengths (Å) and angles (deg): Ta−N01: 2.050(8), Ta−N02: 2.125(8), Ta−P01: 2.581(3), Ta−C1: 2.021(10), Ta−C2: 2.391(11), Ta−C3: 2.295(11), Ta−C4: 2.221(12), C2−C1: 1.470(15), C3−C2: 1.437(15), C4−C3: 1.450(16), N01−Ta−N02: 108.8(3), N01−Ta−P01: 73.1(2), N02−Ta−P01: 75.3(2), C3−C2−C1: 118.8(10), C4−C3−C2: 123.0(10), C1−C2−C3−C4 (dihedral): 23.67

Complex **10** features a five-membered tantallacycle that arises from the coupling of one of the coordinated hexyne carbons to the C_α of the phenylvinyl moiety in **8**. There is evidence of bond delocalization around the four-carbon chain, with the C1−C2, C2−C3, and C3−C4 distances all equal (within experimental error). The exact nature of the bonding between the newly formed four-carbon chain and the tantalum center is complicated; two limiting resonance forms that best describe this bonding motif are shown in Scheme 4. Other workers have synthesized niobium complexes that feature similar metallacyclic structures, and therein the C_4R_5 fragment is described as a *monoanionic* η^3-butadienyl[44] or η^4-butadienyl[45] moiety, depending on the length of the various metal−carbon bonds; in the case of complex **10**, a structure of this type would imply a formally Ta(III) metal center. However, the short Ta−C1 (2.021(10) Å) and Ta−C4 (2.221(12) Å) distances are typical of formal double and single Ta−C bonds, respectively;[74] this, in concert with the solution-state NMR data (*vide infra*), provides compelling evidence for a *trianionic* alkyl−alkylidene ligand coordinated to Ta(V).

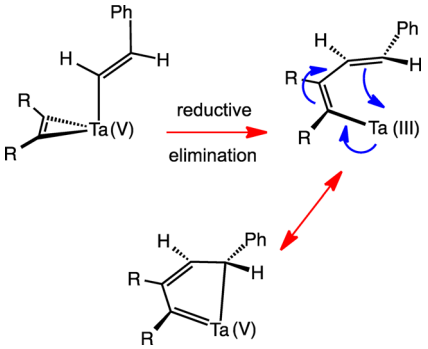
dx.doi.org/10.1021/om500775c | *Organometallics* 2014, 33, 6122−6131

Scheme 4



It is possible to envision the actual C−C bond forming event that gives rise to complex **10** in terms of the reductive elimination of the phenylvinyl unit and one end of the alkenediyl moiety in complex **8**; such a mechanism would necessarily lead to the Ta(III)-butadienyl structure shown in Scheme 4. Nevertheless, as the Ta(V) formalism better matches the spectroscopic and crystallographic data, it is the preferred bonding description for **10**; it is likely that the [^{Ph}NPN*] Ta(III) moiety is strongly reducing and can formally add a pair of electrons to the butadienyl unit, which results in the oxidation to Ta(V), as shown in Scheme 5.

Scheme 5



As was mentioned above, the NMR spectra of **10** are quite complicated as a result of the chiral center that is generated at the terminal carbon of the butadienyl unit; the unsymmetrical nature of **10** is evident in the ^{1}H and ^{13}C{^{1}H} NMR spectra, as there are twice the number of ligand resonances than are present in the spectra of the starting phenylvinyl complex **8**. Similar complexity is observed for **11**, although in this case, the lack of diastereopic methylene groups of the ethyl substituents makes the spectrum less crowded in the 0−5 ppm region. On the basis of the results of a battery of NMR experiments (^{1}H−^{1}H COSY, ^{13}C-APT, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC) it was possible to assign all of these proton resonances; while the full analysis can be found in the Supporting Information, the diagnostic peaks for coupled products in the ^{1}H NMR spectra are the two resonances for the unique, *trans*-disposed protons of the "dienyl" unit: in **10**, they appear at δ 0.61 (dd, $^{3}J_{HH}$ = 8 Hz, $^{2}J_{HP}$ = 3 Hz) and 4.33 (d, $^{3}J_{HH}$ = 8 Hz); in **11**, these resonances are at δ 1.51 (d, $^{3}J_{HH}$ = 9 Hz) and 4.95 (dd, $^{3}J_{HH}$ = 9 Hz, $^{2}J_{HP}$ = 2 Hz). As mentioned above, the extremely downfield chemical shift for C1 (cf. Scheme 4) is typical for a carbene-type carbon (**10**: δ 245.3; **11**: δ 251.4) and lends credence to the Ta(V) alkyl−alkylidene structural motif.

Kinetic Study of the Rearrangement of Complex 8. Although the initial reaction between **4** and phenylacetylene that forms **8** occurs too rapidly to easily monitor by NMR spectroscopy, the subsequent rearrangement of **8** to **10** proceeds slowly enough to permit a study of its kinetic parameters. Based on the linearity of a ln[**8**] versus time plot, the rearrangement was determined to be first order in **8**; details regarding this determination, as well as a discussion of NMR spectrum processing, integral choice, error analysis, and a sample plot of ln[**8**] versus time (at 318 K) used in the determination of k_{obs} can be found in the Supporting Information. From the Eyring plot of ln(k_{obs}/T) versus 1/T, the best fit gave the activation parameters $\Delta H^{\ddagger}$ = 22.2 ± 0.3 kcal/mol and $\Delta S^{\ddagger}$ = −8.7 ± 0.2 cal/(mol)(K). The slightly negative $\Delta S^{\ddagger}$ value is consistent with an ordered transition state for the aforementioned intramolecular rearrangement.

■ CONCLUSIONS

The results of this study illustrate the utility of tantalum alkyne complexes for stoichiometric C−C bond forming reactions. The two reaction sequences featured in this work both involve a migratory insertion step of a Ta(V) hydride species with an aryl isocyanide and phenylacetylene. Although the iminoformyl intermediate could not be detected, in the case of the terminal acetylene, the phenylvinyl species could be characterized via solution-state NMR spectroscopy; depending on the alkyne substituents, the rate of the transformation to the butadienyl species could also be monitored by NMR spectroscopy. In the case of the hexyne derivative **8**, the sequence of reductive elimination followed by internal reduction of the organic fragment by the electron-rich Ta(III) species leads to the observed product, which is best described as an alkyl−alkylidene species. This matches nicely the analogous reaction of the putative iminoformyl species with the alkyne unit, which generates an amido−alkylidene description of the final product. As both imino−formyl alkyne and the phenylvinyl−alkyne complexes undergo C−C bond forming reactions via a formal reductive elimination, it is plausible that these processes are facilitated by the phosphine donor in the NPN ligand set, which stabilizes the lower oxidation state, at least transiently.

■ EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all experiments were conducted by means of standard Schlenk line techniques or in a glovebox (Innovative Technology) equipped with a freezer (−35 °C), under an atmosphere of dry oxygen-free dinitrogen, using oven-dried (200 °C) glassware cooled under dynamic vacuum. Anhydrous hexanes, toluene, diethyl ether, and tetrahydrofuran were purchased from Aldrich, sparged with dinitrogen, and dried further by passage through towers containing activated alumina and molecular sieves. Pentane was refluxed over sodium benzophenone ketal, distilled under positive argon pressure, and degassed via several freeze−pump−thaw cycles. THF-d_8 and C_6D_6 were stirred over sodium benzophenone ketal, vacuum transferred, and freeze−pump−thaw degassed; toluene-d_8 and pyridine-d_5 were stirred over activated molecular sieves and freeze−pump−thaw degassed. KBEt$_3$H (1.0 M in THF) was purchased from Aldrich, evaporated to dryness, and used as a solid. Phenylacetylene was purchased from Aldrich, distilled, degassed, and stored over molecular sieves; phenylacetylene-d_1 was prepared by treating dry phenylacetylene with 1 equiv of ^{n}BuLi and quenching with an excess of DCl (35% w/w in D_2O). Benzyl potassium,[75] [^{Ph}NPN*]H$_2$,[48] Ta(hexyne)Cl$_3$(DME),[19] and Ta(BTA)Cl$_3$(DME)[76] were prepared according to literature methods. NMR spectra were

dx.doi.org/10.1021/om500775c | *Organometallics* 2014, 33, 6122−6131

recorded on a Bruker AV-400 MHz or AV-300 MHz spectrometer. Except where noted, all spectra were recorded at room temperature. ^{1}H NMR spectra were referenced to residual proton signals in C_6D_6 (δ 7.16), toluene-d_8 (δ 2.09), or THF-d_8 (δ 1.73). $^{31}P\{^1H\}$ NMR spectra were referenced to an external sample of $P(OMe)_3$ (δ 141.0 with respect to 85% H_3PO_4 at δ 0.0). $^{13}C\{^1H\}$ NMR spectra were referenced to the solvent resonances of C_6D_6 (δ 128.06), toluene-d_8 (δ 20.9), or THF-d_8 (δ 25.31). Some coupling constants are not assigned bond connectivity because of the inability to make unambiguous assignments; therefore, the actual number of bonds between the two nuclei is not specified. This is especially evident for the phosphorus-31 coupling to aryl protons in the ligand. Elemental analyses were performed using a FISONS 1108 elemental analyzer by Mr. David Wong or Mr. Derek Smith at the Department of Chemistry, University of British Columbia. Electron ionization−mass spectrometry (EI-MS) analyses were performed using a Kratos MS-50 spectrometer (70 eV source) by Mr. Marshall Lapawa at the Department of Chemistry, University of British Columbia.

[^{Ph}NPN*]K$_2$(THF)$_{0.5}$ (1). At room temperature, 30 mL of THF was added to [^{Ph}NPN*]H$_2$ (1.00 g, 1.80 mmol) to give a clear, pale yellow solution. Solid benzyl potassium (468 mg, 3.60 mmol) was added to the solution, and the mixture was left to stir for 30 min. The resulting bright yellow solution was evaporated to dryness and then triturated with 30 mL of hexanes to generate a bright yellow solid. This solid was collected on a sintered-glass frit, washed with hexanes (3 × 30 mL), and dried *in vacuo* to yield 1.10 g (1.74 mmol, 97%). Samples for NMR spectroscopy were prepared in toluene-d_8, with a drop of pyridine-d_5 for additional solubility.

^{1}H NMR (toluene-d_8, 300 MHz): δ 8.06 (bs, 2H), 7.2−6.9 (overlapping resonances, 9H plus residual toluene-d_8), 6.66 (d, J_{HH} = 8 Hz, 2H), 6.07 (dd, J_{HP} = 6 Hz, J_{HH} = 6 Hz, 2H) (ArH), 3.55 (THF, 2H), 2.36 (s, 6H), 2.12 (bs, 12H), 2.04 (s, 6H) ($ArCH_3$), 1.48 (THF, 2H). $^{31}P\{^1H\}$ NMR (toluene-d_8, 120 MHz): δ −25.7 (s). $^{13}C\{^1H\}$ NMR (toluene-d_8, 75 MHz): δ 159.3 (d, J_{CP} = 21 Hz), 152.79, 142.65 (d, J_{CP} = 12 Hz), 136.11, 134.8 (d, J_{CP} = 17 Hz) 131.92, 131.37, 130.52, 130.38, 129.56, 128.28, 126.20, 127.05, 117.68, 115.58, 111.50 (ArC), 67.7, 25.82 (THF), 21.05, 20.59, 20.12, 19.86 ($ArCH_3$). Elemental analysis of **1** was hampered by its pronounced air sensitivity. Despite several attempts, results that were significantly low in carbon were found. The data for one representative attempt are reported: Anal. Calcd for $C_{80}H_{86}K_4N_4O_2P_2$: C, 71.82; H, 6.48; N, 4.19. Found: C, 63.68; H, 6.47; N, 5.40.

[^{Ph}NPN*]Ta(RC≡CR)Cl (R = Et (2); R = SiMe$_3$ (3)). A 200 mL Kontes-seal glass reactor was charged with a magnetic stir bar, **1** (3.57 g, 5.65 mmol), Ta(RC≡CR)Cl$_3$(DME) (**2** = 2.60 g, 5.66 mmol; **3** = 2.75 g, 5.99 mmol)), and 60 mL of THF. The resulting solution was stirred at 54 °C (**2**: 36 h **3**: 6 h), during which the formation of a light-colored precipitate was observed. This suspension was filtered through a pad of silica on a sintered glass frit, and the filtrate was evaporated to dryness *in vacuo* to afford a dark yellow (**2**) or orange (**3**) powder. This powder was triturated with 30 mL of pentane and cooled to −35 °C, whereupon a precipitate formed. This solid (**2**: dark yellow, **3**: dark orange) was collected on a frit, washed with cold pentane (2 × 10 mL), and dried *in vacuo*. (Yields = **2**: 3.47 g, 72%; **3** = 3.78 g, 65%.)

For **2**: ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.62 (bd, J_{HP} = 7.8 Hz, 2H), 7.52 (m, 2H), 7.05 (m, 3H), 6.93 (s, 2H), 6.84 (bd, J_{HH} = 8.7 Hz, 2H), 6.70 (s, 2H), 6.09 (dd, J_{HP} = 5 Hz, J_{HH} = 8.7 Hz, 2H) (ArH), 2.95 (bs, 4H, hexyne CH_2), 2.58 (s, 6H), 2.07 (s, 6H), 2.01 (s, 6H), 1.76 (s, 6H) ($ArCH_3$), 1.03 (bs, 6H, hexyne CH_3). ^{1}H NMR (toluene-d_8, 400 MHz, 298 K): δ 7.57 (bd, J_{HP} = 7.8 Hz, 2H), 7.44 (m, 2H), 7.1−6.9 (overlapping signals, approximately 3 aromatic protons and residual toluene-d_8 protons), 6.87 (s, 2H), 6.77 (bd, J_{HH} = 8.7 Hz, 2H), 6.63 (s, 2H), 5.98 (dd, J_{HP} = 5 Hz, J_{HH} = 8.7 Hz, 2H) (ArH), 2.90 (bs, 4H, hexyne CH_2), 2.51 (s, 6H), 2.05 (s, 6H), 1.99 (s, 6H), 1.68 (s, 6H) ($ArCH_3$), 0.98 (bs, 6H, hexyne CH_3). ^{1}H NMR (toluene-d_8, 400 MHz, 243 K): δ 7.60 (bd, J_{HP} = 7.8 Hz, 2H), 7.47 (m, 2H), 7.1−6.9 (overlapping signals, approximately 3 aromatic protons and residual toluene-d_8 protons), 6.87 (s, 2H), 6.75 (bd, J_{HH} = 8.7 Hz, 2H), 6.64 (s, 2H), 6.05 (dd, J_{HP} = 5 Hz, J_{HH} = 8.7 Hz, 2H) (ArH), 3.49 (q, 2H, $^3J_{HH}$ = 7 Hz, hexyne CH_2), 2.59 (s, 6H, $ArCH_3$), 2.33 (q, 2H, $^3J_{HH}$ = 7 Hz, hexyne CH_2), 2.05 (s, 6H), 1.99 (s, 6H), 1.73 (s, 6H) ($ArCH_3$), 1.27 (t, 3H, J_{HH} = 7 Hz), 0.79 (t, 3H, J_{HH} = 7 Hz) (hexyne CH_3). ^{1}H NMR (toluene-d_8, 400 MHz, 343 K): δ 7.57 (bd, J_{HP} = 7.8 Hz, 2H), 7.44 (m, 2H), 7.1−6.9 (overlapping signals, approximately 3 aromatic protons and residual toluene-d_8 protons), 6.87 (s, 2H), 6.77 (bd, J_{HH} = 8.7 Hz, 2H), 6.63 (s, 2H), 5.98 (dd, J_{HP} = 5 Hz, J_{HH} = 8.7 Hz, 2H) (ArH), 2.90 (bs, 4H, hexyne CH_2), 2.51 (s, 6H), 2.05 (s, 6H), 1.99 (s, 6H), 1.68 (s, 6H) ($ArCH_3$), 0.98 (bs, 6H, hexyne CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 120 MHz): δ 32.4 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 163.10 (d, J_{CP} = 23 Hz), 139.25, 138.48, 136.9 (d, J_{CP} = 32 Hz), 136.1 (d, J_{CP} = 10 Hz), 135.27, 134.19, 132.81 (d, J_{CP} = 9 Hz), 131.15, 130.42, 129.9, 129.6, 129.2, 125.7, 121.8 (d, J_{CP} = 32 Hz), 115.5 (d, J_{CP} = 8 Hz) (ArC), 29.2 (hexyne CH_2), 21.12, 20.28, 20.19, 18.66 ($ArCH_3$), 14.1 (hexyne CH_3). $^{13}C\{^1H\}$ NMR (toluene-d_8, 100 MHz, 243 K): δ 200.6, 182.1 (d, J_{CP} = 2 Hz) (hexyne EtC≡CEt), 163.10 (d, J_{CP} = 32 Hz), 139.05, 137.4, 135.8 (d, J_{CP} = 10 Hz), 135.27, 134.6 (d, J_{CP} = 32 Hz), 134.19, 132.81 (d, J_{CP} = 9 Hz), 131.15, 130.42, 129.9, 129.6, 129.2, 125.6, 121.8 (d, J_{CP} = 32 Hz), 115.3 (d, J_{CP} = 8 Hz) (ArC), 30.6, 26.7 (hexyne CH_2), 21.05, 20.17, 20.165, 18.6 ($ArCH_3$), 15.7, 13.7 (hexyne CH_3). Anal. Calcd for $C_{44}H_{49}Cl_1N_2P_1Ta_1$: C, 61.94; H, 5.79; N, 3.28. Found: C, 61.89; H, 5.87; N, 3.10.

For **3**: ^{1}H NMR (C_6D_6, 300 MHz): δ 7.62 (bd, J_{HP} = 8 Hz, 2H), 7.55 (m, 2H), 7.05 (m, 3H), 6.93 (s, 2H), 6.80 (bd, J_{HH} = 8 Hz, 2H), 6.69 (s, 2H), 6.05 (dd, J_{HP} = 5 Hz, J_{HH} = 9 Hz, 2H) (ArH), 2.48 (s, 6H), 2.12 (s, 6H), 1.98 (s, 6H), 1.73 (s, 6H) ($ArCH_3$), 0.16, (s, 9H) 0.08 (s, 9H) ($Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 120 MHz): δ 29.7 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 225.3, 205.4 (d, J_{CP} = 9 Hz) (TMSC≡CTMS), 161.9 (d, J_{CP} = 30 Hz), 139.5 (d, J_{CP} = 4 Hz), 138.8, 137.3 (d, J_{CP} = 39 Hz), 136.4, 135.2, 134.9 (d, J_{CP} = 2 Hz), 134.2 (d, J_{CP} = 5 Hz), 134.1 (d, J_{CP} = 4 Hz), 131.3, 130.4 (d, J_{CP} = 2 Hz), 130.0 (d, J_{CP} = 5 Hz), 129.7, 128.8 (d, J_{CP} = 10 Hz), 122.6 (d, J_{CP} = 41 Hz), 115.2 (d, J_{CP} = 10 Hz) (ArC), 21.0, 20.5, 20.3, 20.1 ($ArCH_3$), 2.8, 2.0 ($SiCH_3$). Anal. Calcd for $C_{46}H_{57}ClN_2PSi_2Ta$: C, 58.68; H, 6.10; N, 2.98. Found: C, 58.87; H, 6.37; N, 3.30.

[^{Ph}NPN*]Ta(RC≡CR)H (R = Et (4); R = SiMe$_3$ (5)). At room temperature, solid $KHBEt_3$ (164 mg, 1.22 mmol) was added at once to a stirring toluene solution (20 mL) of **2** (1.03 g, 1.20 mmol) or **3** (1.14 g, 1.21 mmol). The resulting (**4**: dark brown, **5**: dark red) solution was stirred for 3 h, during which the formation of a light-colored precipitate was observed. This suspension was filtered through a pad of silica on a sintered glass frit, and the filtrate was evaporated to dryness *in vacuo* to afford a dark brown residue. This residue was triturated with 20 mL of pentane and cooled to −35 °C, whereupon a (**4**: tawny brown, **5**: red) precipitate formed. This solid was collected on a frit, washed with cold pentane (2 × 5 mL), and dried *in vacuo*. (Yields = **4**: 589 mg, 61%, **5** = 493 g, 45%.)

For **4**: ^{1}H NMR (C_6D_6, 400 MHz): δ 21.6 (d, $^2J_{HP}$ = 34.8 Hz, 1H, TaH), 7.71 (d, J_{HP} = 7 Hz, 2H), 7.62 (dd, J_{HP} = 9 Hz, J_{HH} = 6 Hz, 2H), 7.12 (m, 3H), 6.93 (s, 2H), 6.86 (d, J_{HH} = 8 Hz, 2H), 6.67 (s, 2H), 6.00 (dd, J_{HP} = 6 Hz, J_{HH} = 8 Hz, 2H) (ArH), 3.10 (q, J_{HH} = 7 Hz, 2H), 2.78 (q, $^3J_{HH}$ = 7 Hz, 2H) (hexyne CH_2), 2.68 (s, 6H), 2.10 (s, 6H), 2.01 (s, 6H), 1.79 (s, 6H) ($ArCH_3$) 1.16 (t, J_{HH} = 7 Hz, 3H), 0.77 (t, $^3J_{HH}$ = 7 Hz, 3H) (hexyne CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 160 MHz): δ 20.1 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 205.3 (d, J_{CP} = 4 Hz), 184.2 (d, J_{CP} = 11 Hz) (EtC≡CEt), 162.80 (d, J_{CP} = 34 Hz), 141.8, 137.0, 136.3 (J_{CP} = 35 Hz), 135.2, 134.8, 133.4 (d, J_{CP} = 6 Hz), 132.2 (d, J_{CP} = 12 Hz), 129.9 (d, J_{CP} = 3 Hz), 129.69, 129.67, 129.65, 129.60, 129.2 (d, J_{CP} = 9 Hz), 121.81 (d, J_{CP} = 37 Hz), 115.8 (d, J_{CP} = 11 Hz) (ArC), 30.54 (d, J_{CP} = 4.9 Hz), 30.40 (J_{CP} = 2.8 Hz) (hexyne CH_2), 21.43, 20.81, 20.34, 18.72 ($ArCH_3$), 15.75, 14.21 (hexyne CH_3). EI-MS (*m*/*z*): 817 (100, $[M - H]^+$), 735 (40, $[Ta\{^{Ph}NPN^*\}]^+$), 541 (20, $[\{^{Ph}NPN^*\} - Me]^+$). Multiple attempts to obtain acceptable elemental analyses failed; a representative set is shown. Anal. Calcd for $C_{44}H_{50}N_2PTa$: C, 64.54; H, 6.15; N, 3.42. Found: C, 62.71; H, 5.83; N, 3.98.

For **5**: ^{1}H NMR (C_6D_6, 400 MHz): δ 20.6 (d, $^2J_{HP}$ = 35 Hz, 1H, TaH), 7.72 (d, J_{HP} = 7 Hz, 2H), 7.62 (dd, J_{HP} = 8 Hz, J_{HH} = 7 Hz, 2H), 7.02 (m, 3H), 6.91 (s, 2H), 6.82 (bd, J_{HH} = 8 Hz, 2H), 6.61 (s, 2H), 5.92 (dd, J_{HP} = 5 Hz, J_{HH} = 8 Hz, 2H) (ArH), 2.67 (s, 6H), 2.12 (s,

dx.doi.org/10.1021/om500775c | *Organometallics* 2014, 33, 6122−6131

6H), 1.98 (s, 6H), 1.64 (s, 6H) ($ArCH_3$), 0.13, (s, 9H), −0.1 (s, 9H) ($Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 120 MHz): δ 16.3 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz): δ 220.3, 193.2 (d, J_{CP} = 5 Hz) (TMSC≡*C*TMS), 161.9 (d, J_{CP} = 32 Hz), 141.8, 137.6, 136.5, 135.7, 134.9 (d, J_{CP} = 2 Hz), 134.7 (d, J_{CP} = 3 Hz), 133.3 (d, J_{CP} = 12 Hz), 133.2, 131.8, 130.0 (d, J_{CP} = 5 Hz), 129.9 (d, J_{CP} = 5 Hz), 129.6 (d, J_{CP} = 9 Hz), 128.8 (d, J_{CP} = 9 Hz), 123.2 (d, J_{CP} = 35 Hz), 115.3 (d, J_{CP} = 10 Hz) (ArC), 21.1, 20.9, 20.4, 19.5 ($ArCH_3$), 2.3, 0.4 ($SiCH_3$). Multiple attempts to obtain acceptable elemental analyses failed; a representative set is shown. Anal. Calcd for $C_{46}H_{58}N_2PSi_2Ta$: C, 60.91; H, 6.45; N, 3.09. Found: C, 57.10; H, 7.46; N, 2.83

[^{Ph}NPN*]TaC(R)C(R)C(H)N(xylyl) (R = Et (6); R = SiMe$_3$ (7)). To a mixture of **4** (94 mg, 0.11 mmol) or **5** (104 mg, 0.11 mmol) and 2,6-dimethylphenyl isocyanide (15 mg, 0.11 mmol) was added 10 mL of toluene. This solution was stirred for 15 min, after which the volatiles were removed *in vacuo*. The resulting residue (**6**: dark brown, **7**: dark red) was triturated with ∼10 mL of cold pentane and filtered to yield solid **6** (94 mg, 90%) or **7** (102 mg, 86%).

For **6**: ^1H NMR (C_6D_6, 300 MHz): δ 7.38 (dd, J_{HH} = 8 Hz, J_{HP} = 7 Hz, 1H), 7.2−6.6 (15H plus residual C_6D_6 protons), 6.04 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H), 5.91 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H) (ArH), 4.88 (s, 1H, "H3"), 3.38 (dt, $^2J_{HH}$ = 7 Hz, $^3J_{HH}$ = 7 Hz, 1H, "H4a/b"), 2.61 (s, 3H), 2.36 (s, 3H) ($ArCH_3$), 2.29 (m, 1H, "H4a/b"), 2.27 (s, 3H), 2.22 (s, 3H), 2.20 (s, 6H), 1.97 (s, 3H), 1.94 (s, 6H), 1.87 (s, 3H), 1.86 (s, 3H) ($ArCH_3$), 1.60 (m, 1H, "H5a/b"), 1.09 (t, J_{HH} = 7 Hz, "Me2"), 0.77 (m, 1H, "H5a/b") 0.716 (t, J_{HH} = 7 Hz, "Me1"). $^{31}P\{^1H\}$ NMR (C_6D_6, 120 MHz): δ 16.1 (s). $^{13}C\{^1H\}$ (C_6D_6, 75 MHz): δ 231.6 (d, J_{CP} = 30 Hz, C1), 163.7 (d, J_{CP} = 30 Hz), 163.2 (d, J_{CP} = 25 Hz), 151.8, 147.1 (d, J_{CP} = 7 Hz), 146.8 (d, J_{CP} = 3 Hz), 137.2, 136.4, 135.6, 135.4, 134.6, 134.4, 134.2, 133.9, 133.7, 133.6, 133.3, 133.2, 133.0, 132.2, 131.8, 130.2 (d, J_{CP} = 15 Hz), 129.8 (d, J_{CP} = 5 Hz), 129.6, 129.3, 129.2, 128.7, 128.6, 128.4, 127.0 (d, J_{CP} = 5 Hz), 125.2, 120.5 (d, J_{CP} = 35 Hz), 116.8 (d, J_{CP} = 10 Hz), 116.1 (d, J_{CP} = 10 Hz), 113.8 (d, J_{CP} = 36 Hz) (ArC), 111.3 (C2), 93.9 (C3), 29.0 (C5), 21.5, 21.1, 20.8, 20.52 ($ArCH_3$), 20.50 (C6), 20.15, 20.12, 20.10, 20.08, 19.7, 19.0, ($ArCH_3$), 17.7 (Me1), 15.2 (Me2). Anal. Calcd for $C_{53}H_{59}N_3PTa$: C, 67.01; H, 6.26; N, 4.42. Found: C, 67.20; H, 6.24; N, 4.09.

For **7**: ^1H NMR (C_6D_6, 300 MHz): δ 8.22 (dd, J_{HH} = 8 Hz, J_{HP} = 7 Hz, 2H), 7.44 (d, J_{HP} = 7 Hz, 1H), 6.90 (d, J_{HH} = 7 Hz, 1H), 6.75 (m, 4H), 6.63 (d, J_{HH} = 7 Hz, 1H), 6.55 (bs, 2H), 6.31 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H), 6.18 (bs, 1H), 6.03 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H) (ArH), 5.24 (s, 1H, "H3"), 2.20 (s, 6H), 2.09 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.94 (s, 6H), 1.64 (s, 3H), 1.59 (s, 3H) ($ArCH_3$), 0.49 (s, 9H), 0.11 (s, 9H) ($SiCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 120 MHz): δ 28.8 (s). $^{13}C\{^1H\}$ (C_6D_6, 75 MHz): δ 242.6 (C1), 162.0 (d, J_{CP} = 30 Hz), 158.1 (d, J_{CP} = 25 Hz), 148.7 (d, J_{CP} = 7 Hz), 147.5, 146.8 (d, J_{CP} = 7 Hz), 136.4, 135.9, 135.8, 134.8, 134.7, 134.6, 134.55, 134.3, 134.2, 133.9, 133.2, 133.1, 132.3 (d, J_{CP} = 5 Hz), 131.0 (d, J_{CP} = 3 Hz), 130.8, 130.4, 130.3, 130.2, 130.0 (d, J_{CP} = 36 Hz), 129.3, 129.2, 129.0, 128.95, 128.9, 128.6, 128.5, 123. 5, 120.4 (d, J_{CP} = 45 Hz), 120.2 (d, J_{CP} = 7 Hz), 116.7 (d, J_{CP} = 10 Hz), 111.72 (d, J_{CP} = 2 Hz, C2), 111.6 (d, J_{CP} = 36 Hz) (ArC), 107.6 (C3), 22.3, 22.1 (d, J_{CP} = 2 Hz), 21.7, 21.2, 21.2, 20.9, 20.6, 20.5, 20.4, 19.2 ($ArCH_3$), 5.22, 1.14 ($Si(CH_3)_3$). Multiple attempts to obtain acceptable elemental analyses failed; a representative set is shown. Anal. Calcd for $C_{55}H_{67}N_3PSi_2Ta$: C, 63.63; H, 6.50; N, 4.05. Found: C, 65.01; H, 7.09; N, 4.26.

[^{Ph}NPN*]Ta(RC≡CR)(CH═CHPh) (R = Et (8); R = SiMe$_3$ (9)). Phenylacetylene (5 μL, 4.1 mg, 43 umol) was added to a C_6D_6 solution (∼0.5 mL) of **4** (33 mg, 42 umol) or **5** (38 mg, 42 umol), which led to an immediate bright red color change. By NMR, the reaction is quantitative and complete within 5 min.

For **8**: ^1H NMR (C_6D_6, 400 MHz): δ 8.69 (dd, J_{HH} = 18 Hz, J_{HP} = 3 Hz, 1H, TaC*H*═CHPh), 7.65 (d, J_{HH} = 8 Hz, 2H), 7.52 (m, 2H), 7.21 (s, 2H), 7.10 (m, 5H), 6.85 (m, 5H), 6.74 (s, 2H) (ArH), 6.21 (d, J_{HH} = 18 Hz, 1H, TaCH═C*H*Ph), 6.03 (dd, J_{HH} = 8 Hz, J_{HP} = 7 Hz, 2H, ArH), 2.99 (q, J_{HH} = 7.5 Hz, 4H, hexyne CH_2), 2.34 (s, 6H), 2.13 (s, 6H), 2.04 (s, 6H), 1.78 (s, 6H) ($ArCH_3$), 0.99 (t, J_{HH} = 7.5 Hz, 6H, hexyne CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 160 MHz): δ 26.4 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 204.3 (d, J_{CP} = 18 Hz, TaCH═CHPh), 164.1 (d, J_{CP} = 25 Hz), 143.3, 142.0 (TaCH═*C*HPh), 139.3, 137.9 (d, J_{CP} = 5 Hz), 137.1 (d, J_{CP} = 28 Hz), 135.1, 134.7, 132.8 (d, J_{CP} = 9 Hz), 131.1, 130.1, 129.8, 129.5 (d, J_{CP} = 4 Hz), 129.1 (d, J_{CP} = 7 Hz), 128.5, 126.1, 125.6, 121.1 (d, J_{CP} = 28 Hz), 115.7 (d, J_{CP} = 8 Hz) (ArC), 29.2 (bs, hexyne CH_2), 21.1, 20.3, 19.6, 18.7 ($ArCH_3$), 14.6 (bs, hexyne CH_3).

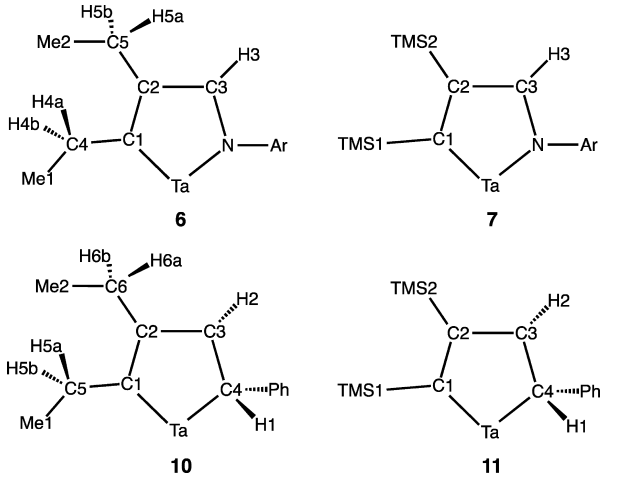


Figure 6. Schematic representation of the core of complexes **6**, **7**, **10**, and **11**. These depictions are only meant to indicate connectivity and serve as an aid for ^1H and $^{13}C\{^1H\}$ NMR spectral assignments; they do not accurately reflect the bonding in the tantallacycles.

For **9**: Due to rapid thermal decomposition (to **11**), this complex was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy only. ^1H NMR (C_6D_6, 300 MHz): δ 8.92 (dd, J_{HH} = 18 Hz, J_{HP} = 3 Hz, 1H, TaC*H*═CHPh), 7.65 (d, J_{HH} = 8 Hz, 2H), 7.5−6.7 (overlapping signals, 16H plus residual C_6D_6 protons) (ArH), 6.03 (dd, J_{HH} = 8 Hz, J_{HP} = 7 Hz, 2H, ArH), 5.83 (d, J_{HH} = 18 Hz, 1H, TaCH═C*H*Ph), 2.32 (s, 6H), 2.09 (s, 6H), 1.97 (s, 6H), 1.78 (s, 6H) ($ArCH_3$), 0.10 (s, 18H, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 160 MHz): δ 23.9 (s).

[^{Ph}NPN*]Ta(EtC≡CEt)(CD═CHPh) (d_1-8). A sample of d_1-**8** was prepared using PhC≡CD and **2**, in a manner identical to that for **8**; the reaction was scaled down by a factor of 10 and performed in a sealed J-Young NMR tube.

^1H NMR (C_6D_6, 400 MHz): δ 7.65 (d, J_{HH} = 8 Hz, 2H), 7.52 (m, 2H), 7.21 (s, 2H), 7.10 (m, 5H), 6.85 (m, 5H), 6.74 (s, 2H) (ArH), 6.20 (bs, 1H, TaCD═C*H*Ph), 6.03 (dd, J_{HH} = 8 Hz, J_{HP} = 7 Hz, 2H, ArH), 2.99 (q, $^3J_{HH}$ = 7.5 Hz, 4H, hexyne CH_2), 2.34 (s, 6H), 2.13 (s, 6H), 2.04 (s, 6H), 1.78 (s, 6H) ($ArCH_3$), 0.99 (t, $^3J_{HH}$ = 7.5 Hz, 6H, hexyne CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 160 MHz): δ 26.7 (s).

[^{Ph}NPN*]TaC(R)C(R)C(H)C(H)Ph (R = Et (10); R = SiMe$_3$ (11)). A 50 mL Kontes-sealed glass reactor was charged with a magnetic stir bar, **2** (300 mg, 0.37 mmol) or **3** (332 mg, 0.37 mmol), phenylacetylene (40 μL, 37 mg, 37 mmol), and 20 mL of toluene. The resulting solution was stirred at 54 °C (**2**: 6 h; **3**: 2 h), during which a brown to red-brown color change was observed. After heating, the volatiles were removed *in vacuo*; the resulting red-brown residue was triturated with ∼20 mL of cold pentane and filtered to yield solid **10** (231 mg, 68%) or **11** (227 mg, 61%).

For **10**: ^1H NMR (C_6D_6, 400 MHz): δ 7.83 (m, 2H), 7.60 (d, J_{HP} = 9 Hz, 1H), 7.45 (d, J_{HP} = 9 Hz, 1H), 7.10 (m, 3H), 6.96 (m, 4H), 6.81 (d, J_{HH} = 8 Hz, 1H), 6.79 (s, 1H), 6.72 (d, J_{HH} = 8 Hz, 1H), 6.69 (s, 1H), 6.57 (s, 1H), 6.21 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H), 5.70 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H), 5.59 (d, J_{HH} = 6.5 Hz, 2H) (ArH), 4.33 (d, J_{HH} = 8 Hz, 1H, "H2"), 3.48 (m, 1H), 2.89 (m, 2H), 2.49 (m, 1H) ("H5a/b, H6a/b") 2.31, 2.15, 2.09, 2.02, 1.94, 1.90, 1.86, 1.62, (s, 3H) ($ArCH_3$), 1.34 (t, J_{HH} = 7.5 Hz, 3H, "Me2"), 0.61 (dd, $^3J_{HH}$ = 8 Hz, $^2J_{HP}$ = 3 Hz, 1H, "H1"), 0.45 (t, J_{HH} = 7.5 Hz, 3H, "Me1"). $^{31}P\{^1H\}$ NMR (C_6D_6, 120 MHz): δ 28.5 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 245.3 (d, J_{CP} = 11 Hz, C1), 168.4 (d, J_{CP} = 32 Hz), 160.4 (d, J_{CP} = 28 Hz), 151.2 (d, J_{CP} = 5 Hz), 147.6, 141.7 (d, J_{CP} = 31 Hz), 137.9, 135.9, 135.6, 134.6, 134.5, 134.4, 133.9, 133.7 (C2), 133.6, 133.5 (d,

dx.doi.org/10.1021/om500775c | *Organometallics* 2014, 33, 6122−6131

J_{CP} = 14 Hz), 133.3, 132.5 (d, J_{CP} = 14 Hz), 131.3 (d, J_{CP} = 25 Hz), 130.9 (d, J_{CP} = 6 Hz), 130.1 (d, J_{CP} = 4 Hz), 129.9 (d, J_{CP} = 3 Hz) 129.6, 129.4, 129.2, 129.1, 129.0, 126.1, 126.0, 125.1 (d, J_{CP} = 42 Hz), 123.2, 117.6 (d, J_{CP} = 34 Hz), 116.7 (d, J_{CP} = 10 Hz), 116.1 (d, J_{CP} = 10 Hz) (ArC), 93.6 (C3), 93.1 (d, J_{CP} = 15 Hz, C4), 31.5 (d, J_{CP} = 6 Hz, C6), 30.4 (C5), 21.2, 20.91, 20.89, 20.6, 20.1, 19.7, 19.1, 18.4 (ArMe), 18.3 (Me1), 16.9 (Me2). Multiple attempts to obtain acceptable elemental analyses failed; a representative set is shown. Anal. Calcd for $C_{52}H_{56}N_2PTa$: C, 67.82; H, 6.13; N, 3.04. Found: C, 60.90; H, 6.22; N, 2.64.

For **11**: ^{1}H NMR (C_6D_6, 300 MHz): δ 8.30 (m, 2H), 7.60 (d, J_{HP} = 9 Hz, 1H), 7.45 (dd, J_{HH} = 7 Hz, J_{HP} = 2 Hz, 1H), 7.33 (dd, J_{HH} = 7 Hz, J_{HP} = 2 Hz, 1H), 7.23 (dt, J_{HH} = 9 Hz, J_{HP} = 2 Hz, 2H), 7.15−6.95 (overlapping multiplets, 5H), 6.76 (t, J_{HH} = 9 Hz, J_{HP} = 2 Hz, 2H), 6.62 (s, 1H), 6.51 (s, 1H), 6.21 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H), 5.70 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H), 6.14 (ddd, J_{HH} = 8.5 Hz, J_{HH} = 5 Hz, J_{HP} = 2 Hz, 2H) (ArH), 4.95 (dd, $^3J_{HH}$ = 9 Hz, $^2J_{HP}$ = 2 Hz, 1H, "H2"), 2.23 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.92 (s, 3H), 1.89 (s, 3H), 1.70 (s, 3H), 1.67 (s, 3H), ($ArCH_3$), 1.51 (d, $^3J_{HH}$ = 9 Hz, 1H, "H1"), 0.38 (s, 9H), 0.15 (s, 9H) ($Si(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 160 MHz): δ 31.9 (s). $^{13}C\{^1H\}$ (C_6D_6, 75 MHz): δ 251.4 (C1), 162.0 (d, J_{CP} = 22 Hz), 156.7 (d, J_{CP} = 18 Hz), 150.9 (d, J_{CP} = 7 Hz), 147.1, 144.9, 135.0 (d, J_{CP} = 9 Hz), 134.9 (d, J_{CP} = 9 Hz), 134.6 (d, J_{CP} = 11 Hz), 134.4 (d, J_{CP} = 20 Hz), 134.3, 133.75, 133.7, 133.0, 132.7, 132.65, 132.3, 131.4, 131.35, 129.8 (d, J_{CP} = 13 Hz), 129.2 (d, J_{CP} = 8 Hz), 129.0, 128.8, 128.65, 128.6, 128.3, 124.6, 122.8 (C2), 119.5 (d, J_{CP} = 5 Hz), 119.1 (d, J_{CP} = 34 Hz), 116.5 (d, J_{CP} = 8 Hz), 115.5 (d, J_{CP} = 27 Hz) (ArC), 104.8 (C4), 98.3 (C3), 21.8, 20.9, 20.7, 20.6, 20.5, 20.4, 20.2, 18.5 ($ArCH_3$), 4.35, 0.36 ($Si(CH_3)_3$). Anal. Calcd for $C_{54}H_{64}N_2PSi_2Ta$: C, 64.27; H, 6.39; N, 2.78. Found: C, 64.07; H, 6.77; N, 3.12.

[^{Ph}NPN*]TaC(Et)C(Et)C(D)C(H)Ph (d_1-10). A sample of d_1-**10** was prepared using PhC≡CD and **2**, in a manner identical to that for **10**; the reaction was scaled down by a factor of 10 and performed in a sealed J-Young NMR tube.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.83 (m, 2H), 7.60 (d, J_{HP} = 9 Hz, 1H), 7.45 (d, J_{HP} = 9 Hz, 1H), 7.10 (m, 3H), 6.96 (m, 4H), 6.81 (d, J_{HH} = 8 Hz, 1H), 6.79 (s, 1H), 6.72 (d, J_{HH} = 8 Hz, 1H), 6.69 (s, 1H), 6.57 (s, 1H), 6.21 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H), 5.70 (dd, J_{HH} = 8 Hz, J_{HP} = 5 Hz, 1H), 5.59 (d, J_{HH} = 6.5 Hz, 2H) (ArH), 3.48 (m, 1H), 2.89 (m, 2H), 2.495 (m, 1H) ("H5a/b, H6a/b") 2.31, 2.15, 2.09, 2.02, 1.94, 1.90, 1.86, 1.62, (s, 3H) ($ArCH_3$), 1.34 (t, J_{HH} = 7.5 Hz, 3H, "Me2"), 0.55 (d, J_{HP} = 3 Hz, 1H, "H1"), 0.45 (t, J_{HH} = 7.5 Hz, 3H, "Me1"). $^{31}P\{^1H\}$ NMR (C_6D_6, 120 MHz): δ 28.5 (s).

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and a CIF file giving full experimental procedures and representative NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: fryzuk@chem.ubc.ca. Fax: +1 604 822-8710. Tel: +1 604 822-2471.

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.D.F. thanks NSERC of Canada for a Discovery Grant, and K.D.J.P. thanks NSERC for Postgraduate Scholarships.

■ REFERENCES

(1) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1981**, *20*, 1285.
(2) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354.
(3) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2352.
(4) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.
(5) Rosenthal, U.; Oehme, G.; Burlakov, V. V.; Petrovskii, P. V.; Shur, V. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *391*, 119.
(6) Nuss, H.; Claiser, N.; Pillet, S.; Lugan, N.; Despagnet-Ayoub, E.; Etienne, M.; Lecomte, C. *Dalton Trans.* **2012**, *41*, 6598.
(7) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans.* **1973**, 977.
(8) Collman, J. P.; Hegedus, L. P. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.
(9) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.
(10) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233.
(11) Cotton, F. A.; Roth, W. J. *Inorg. Chim. Acta* **1984**, *85*, 17.
(12) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.
(13) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.
(14) Hartung, J. B., Jr.; Pedersen, S. F. *Organometallics* **1990**, *9*, 1414.
(15) Arney, D. J.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 1282.
(16) Strickler, J. R.; Bruck, M. A.; Wigley, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 2814.
(17) Oshiki, T.; Nomoto, H.; Tanaka, K.; Takai, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1009.
(18) Strickler, J. R.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 266.
(19) Oshiki, T.; Tanaka, K.; Yamada, J.; Ishiyama, T.; Kataoka, Y.; Mashima, K.; Tani, K.; Takai, K. *Organometallics* **2003**, *22*, 464.
(20) Kaleta, K.; Ruhmann, M.; Theilmann, O.; Beweries, T.; Roy, S.; Arndt, P.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. *J. Am. Chem. Soc.* **2011**, *133*, 5463.
(21) Sun, H.; Burlakov, V. V.; Spannenberg, A.; Baumann, W.; Arndt, P.; Rosenthal, U. *Organometallics* **2002**, *21*, 3360.
(22) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2005**, *24*, 456.
(23) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884.
(24) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Chem.—Eur. J.* **2000**, *6*, 81.
(25) Rosenthal, U.; Burlakov, V. V.; Bach, M. A.; Beweries, T. *Chem. Soc. Rev.* **2007**, *36*, 719.
(26) Straub, B. F.; Bergman, R. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 4632.
(27) Duncan, A. P.; Bergman, R. G. *Chem. Rec.* **2002**, *2*, 431.
(28) Hazari, N.; Mountford, P. *Acc. Chem. Res.* **2005**, *38*, 839.
(29) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708.
(30) Reznichenko, A. L.; Emge, T. J.; Audörsch, S.; Klauber, E. G.; Hultzsch, K. C.; Schmidt, B. *Organometallics* **2011**, *30*, 921.
(31) Severin, R.; Doye, S. *Chem. Soc. Rev.* **2007**, *36*, 1407.
(32) Li, C.; Thomson, R. K.; Gillon, B.; Patrick, B. O.; Schafer, L. L. *Chem. Commun.* **2003**, 2462.
(33) Chamberlain, L. R.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1989**, *8*, 341.
(34) Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. M. *Organometallics* **1990**, *9*, 66.
(35) Hirpo, W.; Curtis, M. D. *Organometallics* **1994**, *13*, 2706.
(36) Gomez, M.; Gomez-Sal, P.; Jimenez, G.; Martin, A.; Royo, P.; Sanchez-Nieves, J. *Organometallics* **1996**, *15*, 3579.
(37) Castro, A.; Galakhov, M. V.; Gomez, M.; Gomez-Sal, P.; Martin, A.; Sanchez, F.; Velasco, P. *Eur. J. Inorg. Chem.* **2000**, 2047.
(38) Sanchez-Nieves, J.; Royo, P.; Mosquera, M. E. G. *Eur. J. Inorg. Chem.* **2006**, 127.

(39) Fandos, R.; Lopez-Solera, I.; Otero, A.; Rodriguez, A.; Ruiz, M. J.; Terreros, P. *Organometallics* **2004**, *23*, 5030.
(40) Galakhov, M. V.; Gomez, M.; Gomez-Sal, P.; Velasco, P. *Organometallics* **2005**, *24*, 848.
(41) Galakhov, M. V.; Gomez, M.; Gomez-Sal, P.; Velasco, P. *Organometallics* **2005**, *24*, 3552.
(42) Herberich, G. E.; Mayer, H. *J. Organomet. Chem.* **1988**, *347*, 93.
(43) Herberich, G. E.; Savvopoulos, I. *J. Organomet. Chem.* **1989**, *362*, 345.
(44) Herberich, G. E.; Mayer, H. *Organometallics* **1990**, *9*, 2655.
(45) Biasotto, F.; Etienne, M.; Dahan, F. *Organometallics* **1995**, *14*, 1870.
(46) Weinert, C. S.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2005**, *24*, 5759.
(47) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668.
(48) MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2005**, *24*, 1112.
(49) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *Organometallics* **1999**, *18*, 4059.
(50) Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. *J. Am. Chem. Soc.* **2001**, *123*, 3960.
(51) Mayer, J. M.; Wolczanski, P. T.; Santarsiero, B. D.; Olson, W. A.; Bercaw, J. E. *Inorg. Chem.* **1983**, *22*, 1149.
(52) Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 2842.
(53) Ignatov, S. K.; Rees, N. H.; Merkoulov, A. A.; Dubberley, S. R.; Razuvaev, A. G.; Mountford, P.; Nikonov, G. I. *Organometallics* **2008**, *27*, 5968.
(54) Mashima, K.; Matsuo, Y.; Tani, K. *Chem. Lett.* **1997**, 767.
(55) Mashima, K.; Matsuo, Y.; Tani, K. *Organometallics* **1999**, *18*, 1471.
(56) Mashima, K.; Matsuo, Y.; Nakahara, S.; Tani, K. *J. Organomet. Chem.* **2000**, *593*−*594*, 69.
(57) Matsuo, Y.; Mashima, K.; Tani, K. *Organometallics* **2002**, *21*, 138.
(58) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1203.
(59) Kloppenburg, L.; Petersen, J. L. *Organometallics* **1997**, *16*, 3548.
(60) Ong, T.-G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1.
(61) Berg, F. J.; Petersen, J. L. *Organometallics* **1989**, *8*, 2461.
(62) Berg, F. J.; Petersen, J. L. *Organometallics* **1991**, *10*, 1599.
(63) Berg, F. J.; Petersen, J. L. *Organometallics* **1993**, *12*, 3890.
(64) Valero, C.; Grehl, M.; Wingbermuehle, D.; Kloppenburg, L.; Carpenetti, D.; Erker, G.; Petersen, J. L. *Organometallics* **1994**, *13*, 415.
(65) Kloppenburg, L.; Petersen, J. L. *Polyhedron* **1995**, *14*, 69.
(66) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73.
(67) Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450.
(68) Jacoby, D.; Isoz, S.; Floriani, C.; Schenk, K.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 4816.
(69) Alvarez, C. M.; Alvarez, M. A.; Garcia, M. E.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **2005**, *24*, 7.
(70) Alvarez, M. A.; Garcia, M. E.; Ramos, A.; Ruiz, M. A. *Organometallics* **2007**, *26*, 1461.
(71) Watanabe, T.; Kurogi, T.; Ishida, Y.; Kawaguchi, H. *Dalton Trans.* **2011**, *40*, 7701.
(72) Clark, J. R.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1233.
(73) Clark, J. R.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1996**, *15*, 3232.
(74) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793.
(75) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed.* **1973**, *12*, 508.
(76) Oshiki, T.; Yamada, A.; Kawai, K.; Arimitsu, H.; Takai, K. *Organometallics* **2007**, *26*, 173.