Addition of Primary and Secondary Phosphines to Dinuclear Tantalum Hydrides: Synthesis of Phosphides and Phosphinidenes via P−H Bond Activation

Michael P. Shaver and Michael D. Fryzuk*

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

Received December 14, 2004

The dinuclear complex (^{RPh}[NPN]Ta)$_2$(μ-H)$_4$ (where ^{RPh}[NPN] = [RP(CH$_2$SiMe$_2$NPh)$_2$] and R = Ph, Cy) shows remarkable reactivity with molecular nitrogen, producing the side-on end-on bound dinitrogen complex (^{RPh}[NPN]Ta)$_2$(μ-η^1:η^2-N$_2$)(μ-H)$_2$. This tantalum tetrahydride also promotes other small molecule activation. Addition of secondary phosphines HPR′$_2$ (R′ = Ph, Cy) to (^{RPh}[NPN]Ta)$_2$(μ-H)$_4$ accesses trihydride phosphide systems (^{RPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PR′$_2$). Addition of primary phosphines H$_2$PR″ (R″ = Cy, Ad) gives bridging phosphinidene tantalum complexes (^{RPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PR″). Molecular structures as determined by X-ray crystallography for the complexes (^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$) and (^{CyPh}[NPN]-Ta)$_2$(μ-H)$_2$(μ-PAd) are presented. Isotopic labeling studies offer mechanistic insights into the reactivity of this tetrahydride system. Reaction of Cy$_2$PH with (^{CyPh}[NPN]Ta)$_2$(μ-D)$_4$, for instance, gives solely the monohydride dideuteride complex (^{CyPh}[NPN]Ta)$_2$(μ-H)(μ-D)$_2$(μ-PCy$_2$). This labeling study indicates that D$_2$ loss forms the reactive species, (^{CyPh}[NPN]Ta)$_2$-(μ-D)$_2$, which promotes small molecule activation. Addition of CyPH$_2$ to (^{CyPh}[NPN]Ta)$_2$(μ-D)$_4$ gives a series of isotopomers, with an average composition of 0.67 H and 1.33 D, supporting a 1,2-H$_2$ elimination step to form the tantalum phosphinidenes. These results are tied into the general reactivity of (^{RPh}[NPN]Ta)$_2$(μ-H)$_4$.

Introduction

Activation of small molecules by metal complexes that contain more than one metal center is a mature area of inorganic chemistry.[1] Interest in this topic continues because of the potential alacrity of such polymetallic systems to engage in cooperative type interactions with extremely stable, small molecules such as N$_2$,[2] CO$_2$,[3] and alkanes.[4] Of particular note are polynuclear metal hydrides that can show enhanced reactivity due to the presence of electron-deficient, bridging hydrides.

In the area of P−H bond activation, there are a number of dinuclear systems that have been shown to react with primary and secondary phosphines. A common outcome is the formation of phosphido-bridged metal complexes by reaction with systems that contain metal−metal multiple bonds.[5,6] Formation of bridging phosphido units by reaction of higher order metal clusters with P−H containing species is also well established.[7−15] Similarly, dinuclear metal hydrides such as (Cp*Fe)$_2$(μ-H)$_4$ undergo P−H bond addition[16] to generate (Cp*Fe)$_2$(μ-H)$_2$(PR$_2$)$_2$, a species with more than one phosphido bridge.

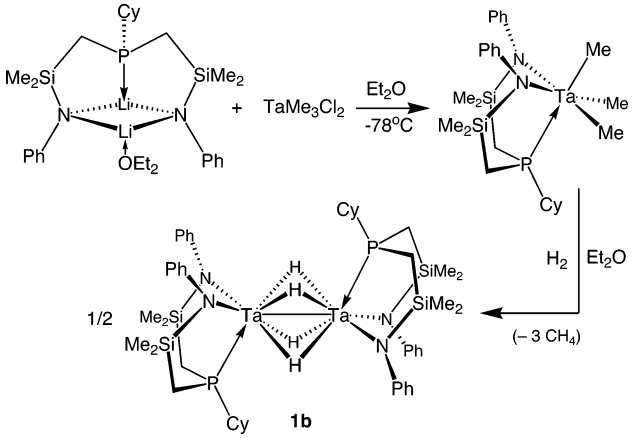
The dinuclear tantalum tetrahydride complex (^{PhPh}[NPN]Ta)$_2$(μ-H)$_4$, **1a** (where ^{PhPh}[NPN] = [PhP(CH$_2$-SiMe$_2$NPh)$_2$]), is a potent reducing agent able to formally reduce dinitrogen by four electrons in the generation of (^{PhPh}[NPN]Ta)$_2$(μ-η^1-η^2-N$_2$)(μ-H)$_2$, a N$_2$ complex with side-on end-on bound dinitrogen.[17,18] This reaction is suspected to occur by initial loss of H$_2$ to generate the reactive, unobserved intermediate (^{PhPh}[NPN]Ta)$_2$-(μ-H)$_2$, **2a**, a d^2−d^2 dimer that formally has a Ta═Ta double bond. To exploit the reducing power of the starting tetrahydride complex, we have examined its characteristic chemistry with a number of small molecules. In this paper, we present the reactions of tetrahydride **1a** and the related cyclohexyl derivative,

* Corresponding author. E-mail: fryzuk@chem.ubc.ca.

(1) Adams, R. D.; Cotton, F. A. *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Wiley-VCH: New York, 1998.
(2) Gambarotta, S.; Scott, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5289−5308.
(3) Doukov, T. I.; Iverson, T. M.; Seravalli, J.; Ragsdale, S. W.; Drennan, C. L. *Science* **2002**, *298*, 567−572.
(4) Matsubara, K.; Inagaki, A.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc.* **1999**, *121*, 7421−7422.
(5) Garcia, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **2002**, *21*, 5515.
(6) Angeles, A. Y.; Garcia, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **2004**, *23*, 433.
(7) Arif, A. M.; Jones, R. A.; Schwab, S. T. *J. Organomet. Chem.* **1986**, *307*, 219.
(8) Blum, T.; Braunstein, P.; Tiripicchio, A.; Tiripicchio, C. M. *Organometallics* **1989**, *8*, 2504.
(9) Caffyn, A. J. M.; Mays, M. J.; Conole, G.; McPartlin, M.; Powell, H. R. *J. Organomet. Chem.* **1992**, *436*, 83.
(10) Don, M. J.; Richmond, M. G.; Watson, W. H.; Nagl, A. *J. Organomet. Chem.* **1989**, *372*, 417.
(11) Ebsworth, E. A. V.; McIntosh, A. P.; Schroder, M. *J. Organomet. Chem.* **1986**, *312*, C41.
(12) Horton, A. D.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1987**, 1557.
(13) Jeffery, J. C.; Lawrence-Smith, J. G. *J. Organomet. Chem.* **1985**, *280*, C34.
(14) King, J. D.; Mays, M. J.; Mo, C. Y.; Solan, G. A.; Conole, G.; McPartlin, M. *J. Organomet. Chem.* **2002**, *642*, 227.
(15) Kwek, K.; Taylor, N. J.; Carty, A. J. *Chem. Commun.* **1986**, 230.
(16) Ohki, Y.; Suzuki, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3120.
(17) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11024.
(18) Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. *J. Am. Chem. Soc.* **2001**, *123*, 3960.

10.1021/om0490076 CCC: $30.25
Publication on Web 03/04/2005

Scheme 1



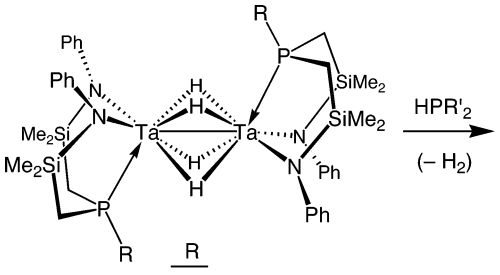
(^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$, **1b** (where ^{CyPh}[NPN] = [CyP(CH$_2$SiMe$_2$NPh)$_2$]), with primary and secondary phosphines. What results from this work are a number of new phosphido-bridged dinuclear species as well as dinuclear phosphinidene derivatives. Evidence is also presented for the formation of the intermediate dihydride species **2**, a key complex proposed in the activation of dinitrogen by **1**.

Results and Discussion

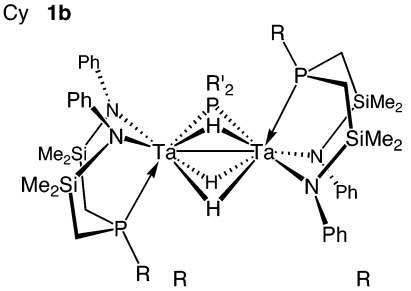
Synthesis of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$. Earlier studies employing the diamidophosphine ligand set, [NPN], have shown that variation of aryl or alkyl groups on the amido and/or phosphine donors can drastically affect complex stability and reactivity.[19,20] In particular, substitution of the phenyl group at phosphorus by cyclohexyl has already been shown to moderate the reactions of complexes that incorporate this modified ligand system as well as promote single-crystal formation in certain cases. For these reasons, we include the synthesis of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$ (**1b**), in which Cy = C_6H_{11}. The sequence of reactions is identical to that previously published preparation of **1a**.[18] Synthesis of ^{CyPh}[NPN]TaMe$_3$ is accomplished by the slow addition of an ethereal solution of ^{CyPh}[NPN]Li$_2$(OEt$_2$) to a cold (−78 °C) solution of TaMe$_3$Cl$_2$ in diethyl ether. The ^{31}P NMR spectrum of ^{CyPh}[NPN]TaMe$_3$ shows a singlet at 16.8 ppm, shifted upfield from 13.5 ppm in ^{PhPh}[NPN]TaMe$_3$. Exposure of a solution of the trimethyl complex to 4 atm of H$_2$ promotes the generation of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$, **1b**, evidenced by a color change from yellow to purple. Upon workup, **1b** is isolated as a bright purple solid in 95% yield. Structure assignment was supported by observation of a singlet at 9.9 ppm in the ^{1}H{^{31}P} NMR spectrum corresponding to four bridging hydrides along with two inequivalent silylmethyl resonances, totalling 24 protons and the requisite cyclohexyl, methylene, and phenyl resonances. A singlet in the ^{31}P{^{1}H} spectrum at 29.2 ppm due to the coordinated phosphine is upfield from the 21.0 ppm peak observed for (^{PhPh}[NPN]Ta)$_2$(μ-H)$_4$. These reactions are shown in Scheme 1.

Synthesis of Tantalum Phosphide Complexes. Addition of dicyclohexylphosphine to an ethereal solution of (^{PhPh}[NPN]Ta)$_2$(μ-H)$_4$, **1a**, under Ar promotes an immediate color change from purple to red along with concomitant gas evolution. Removal of solvent and collection of the pentane-soluble product gave a deep red powder. ^{31}P NMR spectroscopy of this product showed three distinct phosphorus resonances at 10.47, 10.53, and 164.38 ppm. The peak at 164 ppm (P_A) appears as a doublet of doublets coupled to both P_B (73.4 Hz) and P_C (10.1 Hz). P_B (10.53 ppm) appears as a doublet and is assigned *trans* to P_A due to the large coupling constant; it overlaps with a doublet assigned to P_C (10.47 ppm) that exhibits a weaker *cis* coupling. P_A is in the characteristic range for bridging phosphide metal complexes; for example, the heterobimetallic complex Cp$_2$TaH(μ-H)(μ-PPh$_2$)Fe(CO)$_3$ exhibits a ^{31}P chemical shift of 177.2 ppm.[21] The product of **1a** and Cy$_2$PH was initially assigned as (^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$), **3a**.

An analysis of the hydride region of the ^{1}H NMR spectrum supports this assignment. Two distinct hydride environments at 10.5 and 8.7 ppm, integrating to 1H and 2H, respectively, indicate the presence of three bridging hydrides. Further assignment and integration of ^{1}H and ^{31}P NMR spectra confirmed the synthesis of the phosphide complex, **4**, in 84% yield. Other phosphido tantalum complexes can be prepared similarly from the addition of various secondary phosphines to the tantalum tetrahydride complexes **1a** and **1b**. Addition of HPCy$_2$ to **1b**, for example, affords (^{CyPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$), **3b**. ^{31}P NMR spectroscopy of this derivative shows an upfield shift of the phosphide resonance from 164 to 149 ppm. The resonances due to the ligand phosphines shift downfield, appearing at 16.3 and 18.7 ppm. Additions of HPPh$_2$ to **1a** and **1b** afford (^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PPh$_2$), **4a**, and (^{CyPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PPh$_2$), **4b**, respectively. A strong upfield shift of the phosphide resonance also occurs for diphenylphosphine derivatives; these resonances appear at 136.3 ppm for **4a** and 115 ppm for **4b**.



R
Ph **1a**
Cy **1b**



(1)

R
R' = Cy { Ph **3a**, Cy **3b** R' = Ph { Ph **4a**, Cy **4b**

(19) Fryzuk, M. D.; Shaver, M. P.; Patrick, B. O. *Inorg. Chim. Acta* **2003**, *350*, 293.
(20) Shaver, M. P.; Thomson, R. K.; Patrick, B. O.; Fryzuk, M. D. *Can. J. Chem.* **2003**, *81*, 1431.

Table 1. Selected Bond Distances (Å) and Angles (deg) for (^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$), 3a

	length		angle		angle
Ta(1)−N(2)	2.160(4)	N(2)−Ta(1)−N(1)	115.00(14)	N(3)−Ta(2)−Ta(1)	115.41(10)
Ta(1)−N(1)	2.236(4)	N(2)−Ta(1)−P(3)	118.46(11)	N(4)−Ta(2)−Ta(1)	110.73(10)
Ta(1)−P(3)	2.5007(13)	N(1)−Ta(1)−P(3)	86.91(10)	P(3)−Ta(2)−Ta(1)	60.57(3)
Ta(1)−Ta(2)	2.5157(9)	N(2)−Ta(1)−Ta(2)	119.40(10)	N(3)−Ta(2)−P(2)	85.36(11)
Ta(1)−P(1)	2.6031(14)	N(1)−Ta(1)−Ta(2)	119.40(10)	N(4)−Ta(2)−P(2)	79.60(11)
Ta(2)−N(3)	2.114(4)	P(3)−Ta(1)−Ta(2)	58.24(3)	P(3)−Ta(2)−P(2)	86.68(5)
Ta(2)−N(4)	2.185(4)	N(2)−Ta(1)−P(1)	83.65(11)	Ta(1)−Ta(2)−P(2)	146.30(3)
Ta(2)−P(3)	2.4413(14)	N(1)−Ta(1)−P(1)	155.88(4)	C(55)−P(3)−C(49)	107.3(2)
Ta(2)−P(2)	2.5786(13)	P(3)−Ta(1)−P(1)	74.10(10)	C(55)−P(3)−Ta(2)	114.62(14)
P(3)−C(55)	1.925(5)	Ta(2)−Ta(1)−P(1)	118.74(3)	C(49)−P(3)−Ta(2)	120.06(16)
P(3)−C(49)	1.967(5)	N(3)−Ta(2)−N(4)	115.72(15)	C(55)−P(3)−Ta(1)	124.52(15)
P(1)−C(25)	1.790(5)	N(3)−Ta(2)−−P(3)	117.30(11)	C(49)−P(3)−Ta(1)	122.26(16)
P(2)−C(43)	1.852(5)	N(4)−Ta(2)−P(3)	123.58(11)	Ta(2)−P(3)−Ta(1)	61.19(4)

Table 2. Crystallographic Data and Details of Refinement

	(^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$), **3a**	(^{CyPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PAd), **6b**
empirical formula	$C_{60}H_{84}N_4Si_4P_3Ta_2$	$C_{58}H_{91}N_4Si_4P_3Ta_2$
fw	1443.6	1411.5
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
$a-c$ (Å)	13.6335(27), 14.5644(29), 15.7177(31)	17.0490(7), 14.5931(5), 25.6519(9)
α,β,γ (deg)	91.361(30), 90.161(30), 94.016(30)	90.0, 97.550(1), 90.0
V, Å^3	3112.39(20)	6326.81(9)
Z	2	4
D_{calc}, g cm^{-3}	1.54	1.48
μ(Mo Kα), cm^{-1}	3.708	3.646
T, K	173 ± 1	173 ± 1
2θ range (deg)	60.2	55.8
total no. of reflns	13 906	56 050
no. of unique reflns	12 856	13 902
no. of params	678	656
R_1[a]	0.0368	0.037
R_w[a]	0.0872	0.067
goodness-of-fit	1.221	1.173

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2)^{1/2}$.

Interestingly, the phosphide chemical shift has a strong relationship to the nature of the [NPN] ligand phosphine. Employing an alkylphosphine in the ligand backbone results in an upfield shift of 15 and 21 ppm for the additions of $HPCy_2$ and $HPPh_2$, respectively. This upfield shift can be ascribed to the better σ-donor properties of the cyclohexyl-substituted system, which results in a more electron-rich tantalum center to interact with the bridging phosphide.

Attempts were made to detect intermediates in the reaction of the HPR_2 with the tetrahydride. However, the reaction appears to be faster than spectra could be collected. Spectra collected directly after addition of $HPCy_2$ to an NMR tube containing a solution of **1a** (approximately 5 min reaction time) showed no peaks for the starting tetrahydride complex, and no intermediates or decomposition products were detected. This phosphido product is also quite stable, as evidenced by the fact that only after thermolysis of a toluene solution of **3a** at 80 °C for 48 h does it slowly decompose, as evidenced by the formation of the protonated ligand precursor, ^{PhPh}[NPN]H$_2$, as monitored by ^{31}P NMR spectroscopy.

Large deep red crystals of **3a** were grown from a saturated pentane solution and analyzed by X-ray crystallography. An ORTEP[22] depiction of the solid-state molecular structure of **3a** as determined by X-ray crystallography is shown in Figure 1. Relevant bond lengths and angles are listed in Table 1, and crystallographic data are located in Table 2. The molecular

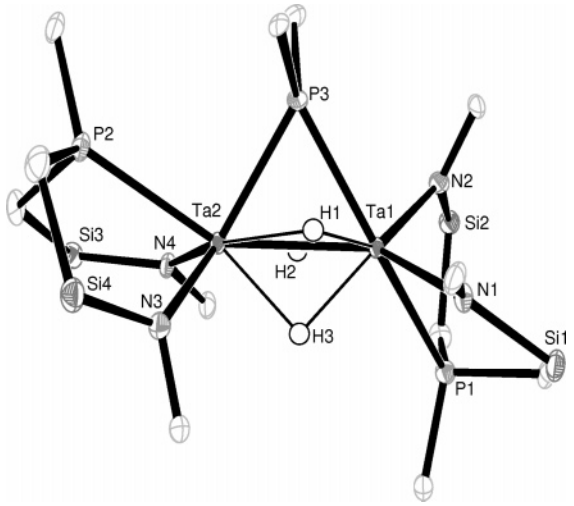


Figure 1. ORTEP drawing (spheroids at 50% probability) of (^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$), **3a**. Silylmethyl, phenyl, and cyclohexyl ring carbons other than *ipso* and methine carbons have been omitted for clarity. Hydrides H(1), H(2), and H(3) were located in the diffraction pattern and refined isotropically.

structure unambiguously shows the bridging phosphide P(3) bound between Ta(1) and Ta(2) at distances of 2.4413(14) and 2.5007(13) Å, respectively, which are considerably shorter than the tantalum phosphine bond lengths of 2.6031(14) Å (Ta(1)−P(1)) and 2.5786(13) Å (Ta(2)−P(2)) as expected for a bridging phosphide. By comparison, the interatomic distances between [NPN] phosphine donors and the tantalum are slightly longer in **3a** than those found in the dinitrogen complex

(21) Boni, G.; Blacque, O.; Sauvageot, P.; Poujaud, N.; Moise, C.; Kubicki, M. M. *Polyhedron* **2002**, *21*, 371.
(22) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Table 3. Shortest Reported Ta−Ta Interatomic Distances and Selected Comparative Examples

complex	d(Ta−Ta), Å
$(Cl_2(PMe_3)_2Ta)_2(\mu\text{-}H)_4$ [25]	2.511(2)
$(^{PhPh}[NPN]Ta)_2(\mu\text{-}H)_3(\mu\text{-}PCy)_2$ [a]	2.5157(9)
$((cu)(PMe_3)_2(H)Ta)_2(\mu\text{-}H)_4$ [26]	2.5359(4)
$(Cl_2(PMe_3)_2Ta)_2(\mu\text{-}H)_2$ [27]	2.545(1)
$([P_2N_2]Ta)_2(\mu\text{-}H)_4$ [28]	2.617(2)
$(Cl_2(PMe_3)_2Ta)_2(\mu\text{-}H)_2(\mu\text{-}Cl)_2$ [29]	2.621(1)
$((\eta^5\text{-}C_5H_4Me)(PPh_2)Ta)_2(\mu\text{-}PPh_2)_2$ [24]	3.024(2)

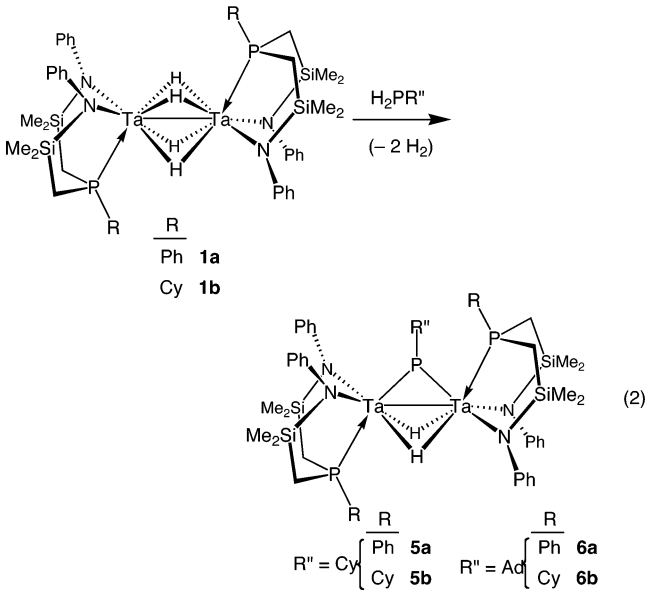
[a] This work.

$(^{PhPh}[NPN]Ta)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}N_2)(\mu\text{-}H)_2$, the latter displaying Ta−P bond distances of 2.573(5) and 2.596(5) Å. Atoms H(1), H(2), and H(3) were located in the diffraction pattern and refined isotropically. To help ascertain the presence of the bridging hydrides, a second crystallographic refinement was performed, where atoms H(1), H(2), and H(3) were deleted from the solution, and the program X-HYDEX[23] was used to predict the location and number of bridging hydrides. The two studies were in agreement with spectroscopic data; three hydrides bridge the two tantalum centers.

The Ta(1)−Ta(2) distance in **3a** is 2.5157(9) Å, which is drastically different from the only other crystallographically characterized example of a dinuclear tantalum phosphide; the complex $((\eta^5\text{-}CpMe)(PPh_2)Ta)_2(\mu\text{-}PPh_2)_2$ has a Ta−Ta bond length of 3.024(2) Å.[24] In fact, **3a** contains one of the shortest reported Ta−Ta single bond distances. The only comparable bond length is found in $(Cl_2(PMe_3)_2Ta)_2(\mu\text{-}H)_4$, with a Ta−Ta bond distance of 2.511(2) Å. Interestingly, crystallographically characterized systems containing the shortest Ta−Ta interatomic distances (Table 3) all contain bridging hydrides. Smaller bridging ligands help bind the two metal centers close together (e.g., halogen-bridged complexes generally have longer Ta−Ta bonds than comparable hydrido-bridged complexes). Also of interest, the complexes with short metal−metal interactions contain at least two phosphine donors supporting the early-metal centers.

Preparation of Tantalum Phosphinidene Complexes. The generation of phosphides from secondary phosphines can be extended to the synthesis of phosphinidenes by using primary phosphines and a similar methodology. Addition of cyclohexylphosphine (H_2PCy) to either **1a** or **1b** produced a similar purple to red color change and gas evolution. Initially, it was suspected that a bridging phosphide would form with a μ-PH(Cy) linkage. ^{31}P NMR studies, however, on the addition of H_2PCy to **1** showed three peaks at 10.9, 15.0, and 448.9 ppm. While the three peaks showed coupling patterns similar to those observed for the tantalum phosphides, the resonance at approximately 450 ppm suggested the presence of a phosphinidene. The ^{31}P chemical shifts for the *trans*-bis(phosphinidene) tantalum complexes $[Cp^*TaCl(\mu\text{-}PR)]_2$ are at 437.6, 482.0, 403.9, and 390.3 ppm for R = Cy, ^{t}Bu, Ph, and Mes, respectively.[24,30] In the ^{1}H NMR spectrum, the observation of a single peak at 10.9 ppm integrating to two equivalent hydrides supports the synthesis of $(^{PhPh}[NPN]Ta)_2(\mu\text{-}H)_2(\mu\text{-}PCy)$, **5a**. Further NMR studies and elemental analysis confirmed this formulation.

Similarly, addition of H_2PCy to **1b** produced $(^{CyPh}[NPN]Ta)_2(\mu\text{-}H)_2(\mu\text{-}PCy)$, **5b**. ^{31}P NMR resonances at 16.6, 22.1, and 436.4 ppm confirmed the generation of a tantalum phosphinidene complex. The downfield resonance appears as a doublet of doublets, coupling strongly to one ligand phosphine and weakly to the other. Two equivalent hydrides are observed in the ^{1}H NMR spectrum at 10.4 ppm. They appear as a 1:1:1:2:1:1:1 septet, coupling to each of the three phosphorus nuclei, giving an overlapping doublet of doublets of doublets. The high solubility of these phosphinidene complexes has prevented characterization by X-ray crystallography. The synthesis of complexes **5a** and **5b** is shown in eq 2.



(2)

Synthesis of phosphinidene tantalum complexes with phenylphosphine proved more difficult. Addition of H_2PPh to **1a** or **1b** resulted in protonation of the amide ligand donors of the starting complex. The only isolable products were the protonated ligands $^{RPh}[NPN]H_2$.

Adamantyl groups have long been used to provide a spherical steric constraint to transition metal systems in order to control reactivity and promote crystallinity.[31−36] For this reason, adamantylphosphine (H_2PAd) was added to solutions of **1a** and **1b**. These reactions gave the corresponding phosphinidene com-

(23) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.
(24) Abdul-Hadi, G. A.; Fromm, K.; Blaurock, S.; Jelonek, S.; Hey-Hawkins, E. *Polyhedron* **1997**, *16*, 721.
(25) Scioly, A. J.; Luetkens, M. L.; Wilson, R. B.; Huffman, J. C.; Sattelberger, A. P. *Polyhedron* **1987**, *6*, 741.
(26) Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1992**, *11*, 1559.
(27) Wilson, R. B.; Sattelberger, A. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 858.
(28) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *Organometallics* **2000**, *19*, 3931.
(29) Sattelberger, A. P.; Wilson, R. B.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 4179.
(30) Blaurock, S.; Hey-Hawkins, E. *Eur. J. Inorg. Chem.* **2002**, 2975.
(31) Soo, H. S.; Diaconescu, P. L.; Cummins, C. C. *Organometallics* **2004**, *23*, 498.
(32) Tsang, W. C. P.; Jernelius, J. A.; Cortez, G. A.; Weatherhead, G. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2591.
(33) Blaurock, S.; Hey-Hawkins, E. *Zeit. Anorg. Allg. Chem.* **2002**, *628*, 2515.
(34) Tellini, V. H. S.; Jover, A.; Galantini, L.; Meijida, F.; Tato, J. V. *Acta Crystallogr.* **2004**, *B60*, 204.
(35) Grubb, T. L.; Mathias, L. J. *J. Polym. Sci. A.: Polym. Chem.* **2000**, *35*, 1743.

Table 4. Selected Bond Distances (Å) and Angles (deg) for (^{CyPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PAd), 6b

	length		angle		angle
Ta(1)−N(2)	2.084(3)	N(2)−Ta(1)−N(1)	111.38(12)	N(4)−Ta(2)−P(3)	117.14(9)
Ta(1)−N(1)	2.085(3)	N(2)−Ta(1)−P(3)	103.18(9)	N(3)−Ta(2)−Ta(1)	117.82(8)
Ta(1)−P(3)	2.3394(9)	N(1)−Ta(1)−P(3)	101.38(8)	N(4)−Ta(2)−Ta(1)	114.65(8)
Ta(1)−Ta(2)	2.7532(2)	N(2)−Ta(1)−Ta(2)	123.93(8)	P(3)−Ta(2)−Ta(1)	53.44(2)
Ta(1)−P(1)	2.6479(9)	N(1)−Ta(1)−Ta(2)	122.93(8)	N(3)−Ta(2)−P(2)	78.75(9)
Ta(2)−N(3)	2.094(3)	P(3)−Ta(1)−Ta(2)	55.60(2)	N(4)−Ta(2)−P(2)	77.21(9)
Ta(2)−N(4)	2.080(3)	N(2)−Ta(1)−P(1)	81.67(9)	P(3)−Ta(2)−P(2)	95.33(3)
Ta(2)−P(3)	2.4030(9)	N(1)−Ta(1)−P(1)	82.56(8)	Ta(1)−Ta(2)−P(2)	148.77(2)
Ta(2)−P(2)	2.6069(9)	P(3)−Ta(1)−P(1)	171.91(3)	Ta(2)−P(3)−C(49)	140.41(11)
P(3)−C(49)	1.883(3)	Ta(2)−Ta(1)−P(1)	116.33(2)	Ta(1)−P(3)−C(49)	148.21(11)
P(1)−C(13)	1.853(4)	N(3)−Ta(2)−N(4)	113.10(12)	Ta(2)−P(3)−Ta(1)	70.96(3)
P(2)−C(31)	1.849(4)	N(3)−Ta(2)−P(3)	126.57(9)	∑P(3) angles	359.58

plexes (^{PhPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PAd), **6a**, and (^{CyPh}[NPN]-Ta)$_2$(μ-H)$_2$(μ-PAd), **6b**, in 90% and 95% yield, respectively (eq 2). Characterization of **6a** and **6b** by NMR showed patterns similar to the reaction of cyclohexylphosphine with tantalum hydrides. For each phosphinidene, three resonances were observed in ^{31}P{^{1}H} spectra: 7.35, 10.23, and 474.26 ppm for **6a** and 14.37, 19.80, and 468.35 ppm for **6b**.

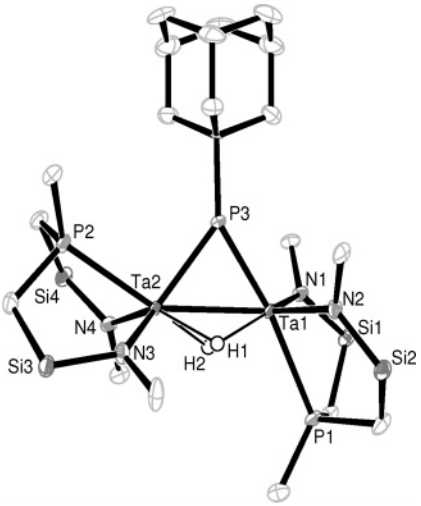


Figure 2. ORTEP drawing (spheroids at 50% probability) of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PAd), **6b**. Silylmethyl, phenyl, and cyclohexyl ring carbons other than *ipso* and methine carbons have been omitted for clarity. Hydrides H(1) and H(2) were located in the diffraction pattern and refined isotropically.

As was observed in phosphide systems, the choice of phosphine in the [NPN] ancillary ligand produces a marked effect in phosphinidene chemical shift. Systems stabilized by the ^{CyPh}[NPN] ligand appear upfield by 12 ppm for the addition of H_2PCy to the tantalum hydrides. The effect is somewhat muted for adamantyl phosphine: an upfield shift of 6 ppm is observed.

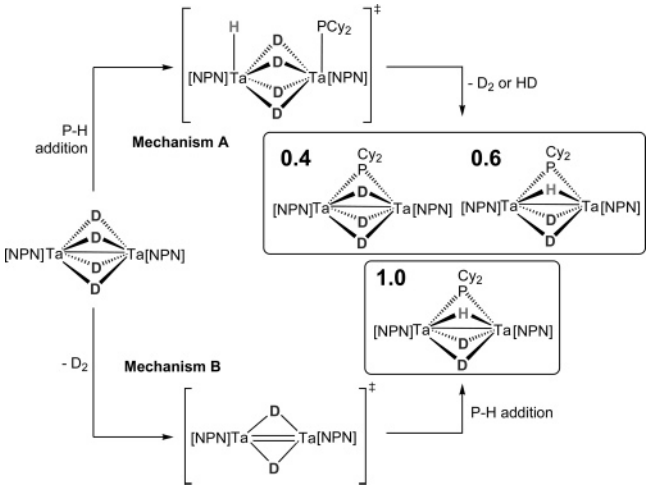
Dark red crystals of **6b** were grown from pentane solutions and were studied by X-ray crystallography. An ORTEP[22] depiction of the solid-state molecular structure of **6b** as determined by X-ray crystallography is shown in Figure 2. Relevant bond lengths and angles are listed in Table 3, and crystallographic data are located in Table 2. The bridging phosphinidene P(3) has Ta(1)−P(3) and Ta(2)−P(3) bond lengths of 2.3394(9) and 2.4030(9) Å, respectively, shortened significantly from the phosphide derivative. P(3) is also quite planar; the sum of angles Ta(1)−P(3)−Ta(2), Ta(1)−P(3)−C(48), and Ta(2)−P(3)−C(48) is 359.59°. The molecular structure clearly supports the assignment of a phosphinidene bridge.

The tantalum bonds to ligand phosphines P(1) and P(2) have lengthened again to 2.6069(9) and 2.6479(9) Å, respectively. The metal−metal bond has also lengthened considerably, from 2.5157(9) Å in **3a** to 2.7532(2) Å in **6b**. Presumably, eliminating one bridging hydride from the system also removes some of the geometric constraints that induced such a short Ta−Ta interatomic distance in structure **3a**. Hydride locations were again confirmed by two methods: isotropic refinement of diffraction pattern locations and using X-HYDEX.[23] Structures **3a** and **6b** are rare examples of structurally characterized dinuclear tantalum complexes bridged by a single phosphide or phosphinidene.

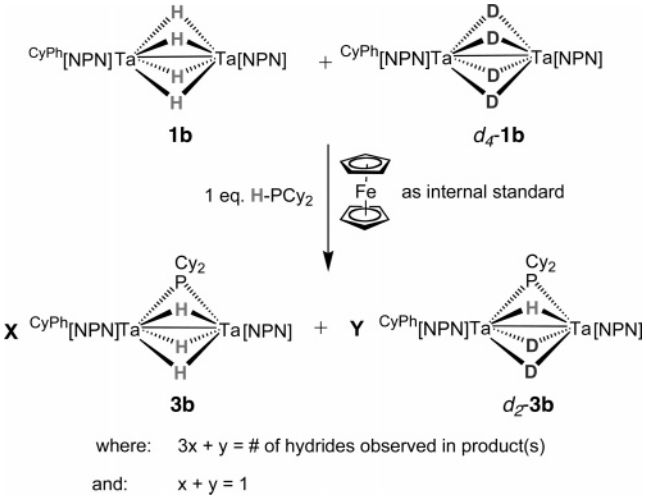
Mechanistic Studies. Addition of primary and secondary phosphines to the tantalum hydrides **1a** and **1b** clearly demonstrates that these complexes can promote reactivity in addition to dinitrogen activation. The initial premise behind the H−P additions focused on exploiting the reactivity of the putative Ta=Ta double bond in ($^{RR'}$[NPN]Ta)$_2$(μ-H)$_2$, formed as a reactive, but undetected intermediate. To support this idea, the mechanism of P−H addition in the synthesis of the tantalum phosphide and phosphinidene complexes was examined by analysis of product distributions using isotopic labeling studies on the addition of H_nPR_{3-n} (n = 1, 2) to (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$. The deuterated isotopomer (^{CyPh}[NPN]Ta)$_2$(μ-D)$_4$, d_4-**1b**, was prepared by modifying the synthesis of **1b**, employing D_2 gas instead of H_2 gas. Spectroscopic characterization of deuteride d_4-**1b** showed little deviation from spectra for the corresponding hydride complex, except the disappearance of hydride resonances at 9.9 ppm. As will be seen, reaction pathways can be supported by integration of the hydride region in ^{1}H NMR spectra following reaction of phosphines with the tetradeuteride complex d_4-**1b**. Any observed hydrides must originate from the primary or secondary phosphines, and the presence or absence of these peaks can indicate whether D_2, H_2, or HD is lost during the reaction. This assumes that the isotope scrambling from the ancillary substituents does not occur. Cursory experiments using the analogous phenyl-substituted phosphine system d_4-**1a** showed identical patterns; one example is explicitly mentioned below. However, the main discussion focuses on the cyclohexyl-substituted phosphine system.

(36) Gessmann, R.; Petratos, K.; Hanodrakas, S. J.; Tsitsa, P.; Antoniadou-Vyza, E. *Acta Crystallogr.* **1992**, *C48*, 347.

Scheme 2



Scheme 3



Two mechanisms are proposed for the addition of dicyclohexylphosphine to **1a** or **1b** that differ only in the step where H_2 or D_2 is eliminated. In mechanism A, P−H addition across the Ta−Ta single bond in d_4-**1b** would give a phosphide-monohydride-tetradeuteride intermediate, as shown in Scheme 2. Loss of either D_2 or HD from this species would generate the final product. Statistically, there are 10 different eliminations possible, forming two isotopomers; six of these would eliminate D_2 and leave H in the resultant product. In other words, there is a 60% possibility that D_2 will be lost instead of HD. This analysis assumes that the re-addition of D_2 or HD does not occur.

Mechanism B proposes that D_2 loss precedes P−H addition. Loss of D_2 followed by P−H addition generates the final product. Thus, only D_2 would be lost, forming a dideuteride intermediate with a Ta−Ta double bond. P−H addition would give a single isotopomer: the hydride from the phosphine addition would appear in the final product 100% of the time.

Specifically not considered is the prior association of the primary or secondary phosphine with the tetradeuteride d_4-**1b** or with dideuteride d_2-**3** as a neutral donor. While such adducts are likely, our isotopic labeling experiments do not provide any evidence of their participation. However, there is some precedent for such a species; sodium−mercury amalgam reduction of the complex $(Cl_2(PMe_3)_2Ta)_2(\mu\text{-}H)_2(\mu\text{-}Cl)_2$ gives $(Cl_2(PMe_3)_2Ta)_2(\mu\text{-}H)_2$, a dihydride dinuclear Ta(III) complex with a metal−metal double bond. This species can be hydrogenated to generate $(Cl_2(PMe_3)_2Ta)_2(\mu\text{-}H)_4$, a complex isoelectronic to **1**.[25]

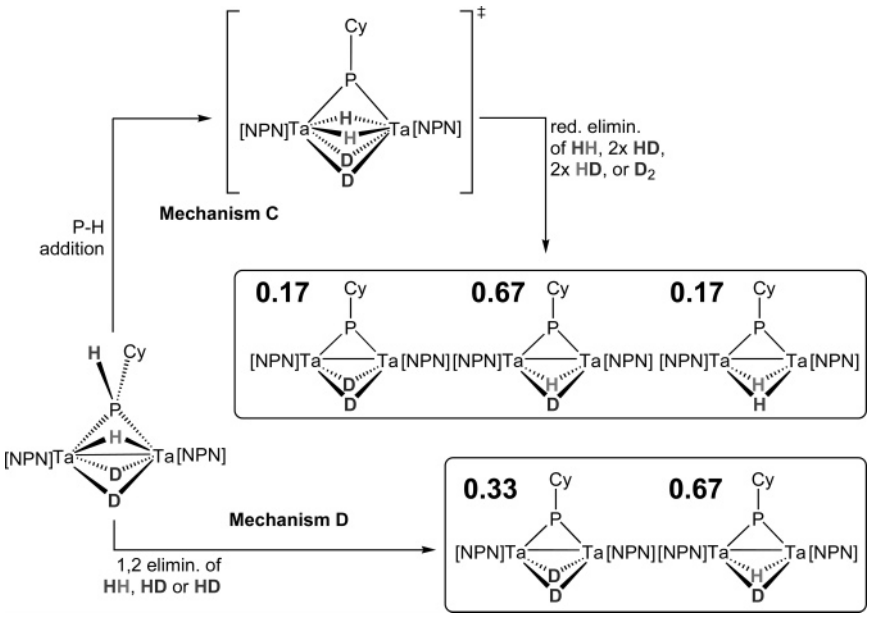
Experimentally, addition of Cy_2PH to a C_6D_6 solution of d_4-**1b** in an NMR tube fitted with a rubber septum allows for monitoring of this reaction by NMR spectroscopy. The observed spectra are similar to **3b**, except for the hydride region. Careful integration of the two hydride resonances supports the formation of a monohydride-dideuteride complex. Relative to a silylmethyl proton peak (3H), the peak at δ 8.67 integrates to 0.65H and the peak at δ 10.47 integrates to 0.33H, totaling 0.98H. Similar results were observed for the addition of Cy_2PH to d_4-**1a** (δ 8.56, 0.63H; δ 10.35, 0.33H). In both cases, the hydride from P−H addition is not lost as HD; the transfer is quantitative. The formation of $(^{CyPh}[NPN]Ta)_2(H)(D)_2(PCy_2)$, d_2-**3b**, supports mechanism B. Loss of D_2 generates a Ta═Ta double bond, which is the reactive intermediate in this hydrophosphination reaction.

To employ complex d_4-**1b** to make mechanistic conclusions based on observed product distributions, the presence of a kinetic isotope effect in the hydrophosphination reactions was examined. To accomplish this, the following experiment shown in Scheme 3 was devised: addition of 1 equiv of Cy_2PH to $(^{CyPh}[NPN]Ta)_2(\mu\text{-}H)_4$, **1b**, and $(^{CyPh}[NPN]Ta)_2(\mu\text{-}D)_4$, d_4-**1b**, would give respectively $(^{CyPh}[NPN]Ta)_2(\mu\text{-}H)_3(\mu\text{-}PCy_2)$, **3b**, and $(^{CyPh}[NPN]Ta)_2(\mu\text{-}D)_2(\mu\text{-}H)(\mu\text{-}PCy_2)$, d_2-**3b**. This competition experiment will determine if the tetrahydride and its deuterated isotopomer react at different rates and thus exhibit a measurable kinetic isotope effect. Equimolar amounts of **1b** and d_4-**1b** were added to an NMR tube containing ferrocene as an internal standard, a solution of $HPCy_2$ in C_6D_6 was subsequently added via syringe through a rubber septum, and the reaction was monitored by NMR spectroscopy. The reaction to form **3b** and d_2-**3b** is much faster than any isotopic exchange reactions between **1b** and d_4-**1b**.

Integration of the hydride resonances at δ 8.67 and 10.47 against the ferrocene internal standard totals 2.07H. With simple algebra, one can now solve for the ratio of **3b** and d_2-**3b** produced during the reaction. If x is the amount of **3b** that has formed and y is the amount of d_2-**3b** formed, then the sum of the hydride integrations must be $3x + y$. As only 1 equiv of phosphine was added into the mixture, $x + y = 1$. Solving for x and y reveals the products formed in 53.5% and 46.5% yield, respectively. If complexes **1b** and d_4-**1b** reacted at the same rate, a 50/50 ratio of products should be observed. While a minor kinetic isotope effect is observed, the slight difference does not account for the quantitative transfer of hydride to form phosphides in the previous experiment. With confidence, one can now propose that the formation of tantalum phosphides proceeds through a dideuteride complex, as shown in mechanism B. Indirectly, the observation of a small isotope effect in this competition experiment suggests that the rate-determining step occurs prior to P−H addition.

Generation of phosphinidene tantalum complexes presents another mechanistic question. For the addition of a primary phosphine to d_4-**1b**, the first step can be

Scheme 4



assumed to proceed analogously to mechanism B, again presuming readdition of H_2, HD, or D_2 does not occur. From this monohydride-dideuteride tantalum complex, there are again two possible pathways to tantalum phosphinidenes. The addition of the remaining P−H bond across the latent Ta−Ta single bond would form an intermediate complex with two hydrides, two deuterides, and a bridging phosphinidene. Elimination of H_2, HD, or D_2 from this complex would generate the observed tantalum phosphinidene. This potential mechanism is shown in Scheme 4 as mechanism C. In this case, the potential elimination of H_2 (16.7%), HD (66.7%), and D_2 (16.7%) would generate three isotopomers. On average, one hydride would remain in the final product. If mechanism C is in action, a monohydride-monodeuteride isotopic composition, ($^{RR'}$[NPN]-Ta)$_2$(μ-H)(μ-D)(μ-PCy), would be observed.

Alternatively, 1,2-H_2 elimination could happen prior to P−H addition, as shown by mechanism D in Scheme 4. The P−H bond and a tantalum hydride or deuteride could eliminate in a concerted fashion to give the observed product. In this case, only loss of H_2 or HD is possible and would lead to the formation of two isotopomers with an average isotopic composition of 0.67 H and 1.33 D. Integration of the hydride region would show 0.67 H if mechanism D was operating. This mechanism has some support in the literature: a 1,2-H_2 elimination has been proposed for the decomposition of (silox)$_3$TaH(PHPh) to (silox)$_3$Ta=PPh.[37] In this case, only 1,2-H_2 elimination could occur, as the Ta(V) complex cannot be further oxidized. This would preclude the P−H oxidative addition step proposed in mechanism C.

Experimentally, addition of H_2PCy to d_4-**1b** is analogous to the previous isotopic labeling studies. In this case, the spectrum shows only one peak in the hydride region at δ 10.87 that integrates to 0.65H relative to 24 silylmethyl protons. The product formed in this reaction is a mixture of two isotopomers with an average composition of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_{0.67}$(μ-D)$_{1.33}$(μ-PCy), d_x-**6b**. Similarily, addition of CyPH$_2$ to d_4-**1a** supports these results (δ 10.47, 0.69H). If the product contains only two-thirds of a hydride on average, mechanism D may be operating, presuming a negligible kinetic isotope effect. The concerted 1,2-H_2 elimination from Ta−H and P−H bonds generates the phosphinidene complex.

These experimental results rule out another mechanism not explicitly detailed in Scheme 4. After phosphide formation, if release of HD or D_2 occurs prior to P−H addition, then one would predict a mixture of (^{CyPh}[NPN]Ta)$_2$(μ-H)(μ-D)(μ-PCy), d_1-**6b**, and (^{CyPh}[NPN]-Ta)$_2$(μ-H)$_2$(μ-PCy), **6b**, with hydride resonances integrating to 1.5H, clearly at odds with the observed formation of products with 0.67 ± 0.02H.

Concluding Remarks

Reactions of primary and secondary phosphines with [NPN]-supported dinuclear tantalum tetrahydride complexes readily access bridging phosphido and phosphinidene compounds via P−H bond activation. The formation of the phosphide-trihydride derivatives ([NPN]Ta)$_2$(μ-H)$_3$(μ-PR$_2$) is consistent with initial loss of H_2 from the tetrahydride ([NPN]Ta)$_2$(μ-H)$_4$ via reductive elimination to generate the unobserved Ta=Ta intermediate, ([NPN]Ta)$_2$(μ-H)$_2$; this is followed by oxidative addition of a P−H bond across the Ta=Ta double bond. In the case of primary phosphines, phosphinidene complexes ([NPN]Ta)$_2$(μ-H)$_2$(μ-PR) are generated by a 1,2-H_2 elimination following formation of the phosphide-trihydride intermediate. By probing these reactions using isotopic labeling studies, information on the intimate details of these processes has been obtained.

Experimental Section

General Considerations. Unless otherwise stated, all manipulations were performed under an inert atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques. Where choice of atmosphere affects reaction outcomes, the distinction between dinitrogen

(37) Bonanno, J. B.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1994**, *116*, 11159.

and argon use will be made. Anhydrous hexanes and toluene were purchased from Aldrich, sparged with dinitrogen, and passed through activated alumina and Ridox catalyst columns under a positive pressure of nitrogen prior to use.[38] Anhydrous pentane, benzene, tetrahydrofuran, and diethyl ether were purchased from Aldrich, sparged with dinitrogen, and passed through an Innovative Technologies Pure-Solv 400 solvent purification system. All organic solvents were tested with addition of a toluene solution of sodium benzophenone ketyl prior to use to ensure absence of oxygen and water. Alternatively, anhydrous diethyl ether was stored over sieves and distilled from sodium benzophenone ketyl under argon. Tetrahydrofuran was refluxed over CaH_2 prior to distillation from sodium benzophenone ketyl under argon, and pentane was stored over sieves and distilled from sodium benzophenone ketyl solublized by tetraglyme under argon prior to storage over a potassium mirror. Nitrogen gas was dried and deoxygenated by passage through a column containing activated molecular sieves and MnO. Deuterated benzene was dried by heating at reflux with sodium/potassium alloy in a sealed vessel under partial pressure, then trap-to-trap distilled, and freeze−pump−thaw degassed three times. Unless otherwise stated, ^{1}H, ^{31}P, ^{1}H{^{31}P}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AMX-500 instrument with a 5 mm BBI probe operating at 500.1 MHz for ^{1}H. ^{1}H NMR spectra were referenced to residual protons in C_6D_5H (δ 7.15 ppm) with respect to tetramethylsilane at δ 0.0 ppm. ^{31}P NMR spectra were referenced to either external or internal $P(OMe)_3$ (δ 141.0 ppm with respect to 85% H_3PO_4 at δ 0.0 ppm). Elemental analyses were performed by Mr. M. Lakha of the University of British Columbia, Department of Chemistry. Selected complexes in this paper do not have elemental analysis data due to problems with sample handling and the high air- and nitrogen-sensitivity of these complexes. Complexes (^{PhPh}[NPN]Ta)$_2$(μ-H)$_4$,[18] $TaCl_2Me_3$,[39] ^{CyPh}[NPN]$Li_2(OEt_2)$,[19] H_2PPh,[40] and H_2PAd[41,42] were prepared by literature procedures. H_2PCy was purchased from Strem and distilled under N_2 prior to use. All other reagents were purchased from Aldrich and used as supplied.

Preparation of ^{CyPh}[NPN]TaMe$_3$. A solution of $TaMe_3Cl_2$ (5.00 g, 16.84 mmol) in 50 mL of Et_2O was added dropwise to a solution of ^{CyPh}[NPN]$Li_2(OEt_2)$ (8.90 g, 16.84 mmol) in 800 mL of Et_2O at −78 °C. The solution was then warmed to room temperature and a white precipitate appeared. The solution was evaporated to dryness, and the remaining solids were extracted into 50 mL of toluene and filtered through Celite. The solvent was removed, and the solids were washed with pentane to afford a yellow solid, ^{CyPh}[NPN]TaMe$_3$, in 85% yield (9.54 g, 14.31 mmol). ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.22 (s, 6H, SiCH_3), 0.01 (s, 6H, SiCH_3), 0.61 (s, 9H, TaCH_3), 0.63−1.75 (m, 15H, C_6H_{11}, PCH_2Si), 6.65−6.80 (m, 6H, NPh), 6.95−7.05 (m, 4H, NPh). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 16.78 (s). Anal. Calcd for $C_{27}H_{46}N_2PSi_2Ta$: C, 48.64; H, 6.95; N, 4.20. Found: C, 48.45; H, 6.67; N, 4.60.

Preparation of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$, 1b. A solution of ^{CyPh}[NPN]TaMe$_3$ (2.50 g, 3.75 mmol) in 50 mL of Et_2O was transferred into a 200 mL thick-walled glass vessel equipped with a Kontes valve and thoroughly degassed via three freeze−pump−thaw cycles. The vessel was cooled in liquid nitrogen and H_2 gas added. The vessel was sealed, warmed to room temperature, and stirred for 24 h, over which time the solution turned to deep purple. The solvent was removed in vacuo, and the product extracted into degassed pentane and filtered through Celite. Removal of pentane affords (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$ in 97% yield (2.27 g, 1.82 mmol). The product was highly nitrogen-sensitive in solution, but is stable under nitrogen in solid form at −35 °C. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ 0.18 (s, 12H, SiCH_3), 0.24 (s, 12H, SiCH_3), 0.35−1.90 (m, 30H, C_6H_{11}, PCH_2Si), 6.96 (s, 4H, NPh), 7.18 (s, 8H, NPh), 7.36 (s, 8H, NPh), 9.90 (s, 4H, TaHTa). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 29.20 (s). Anal. Calcd for $C_{27}H_{46}N_2PSi_2Ta$: C, 46.22; H, 6.30; N, 4.49. Found: C, 45.89; H, 6.20; N, 4.34.

Preparation of (^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$), 3a. The following procedure is representative of the synthesis of compounds **3** and **4**. A solution of (^{PhPh}[NPN]Ta)$_2$(μ-H)$_4$ (500 mg, 0.405 mmol) in 20 mL of Et_2O under Ar was prepared in a vessel equipped with a Kontes valve. Dicyclohexylphosphine (80.3 mg, 0.405 mmol) was added to the flask via microsyringe, the vessel was sealed, and its contents were stirred for 30 min. A color change from deep purple to red was observed, along with the evolution of a gas. Removal of solvent in vacuo left a red, oily solid. This solid was triturated with pentane and dried under vacuum to afford (^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$) as a red powder in 95% yield (551 mg). Crystals of **3a** suitable for X-ray diffraction were grown from slow evaporation of a concentrated solution of the phosphide in layered benzene/HMDS. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.21 (s, 3H, SiCH_3), −0.02 (s, 3H, SiCH_3), 0.07 (s, 3H, SiCH_3), 0.17 (s, 3H, SiCH_3), 0.23 (s, 3H, SiCH_3), 0.31 (s, 3H, SiCH_3), 0.88−2.65 (m, 30H, C_6H_{11}, PCH_2-Si), 6.65−7.62 (m, 30H, NPh, PPh), 8.67 (m, 2H, TaHTa), 10.47 (m, 1H, TaHTa). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 10.47 (d, $^2J_{PP}$ = 12 Hz) 10.53 (d, $^2J_{PP}$ = 83 Hz), 164.38 (d of d, $^2J_{PP}$ = 12 Hz, 83 Hz). Anal. Calcd for $C_{60}H_{87}N_4P_3Si_4Ta_2$: C, 50.34; H, 6.13; N, 3.91. Found: C, 50.09; H, 6.20; N, 4.34.

Preparation of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$), 3b. This reaction was conducted analogously to the synthesis of **3a**. (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$ (500 mg, 0.401 mmol) and dicyclohexylphosphine (79.49 mg, 0.401 mmol) were employed to afford (^{CyPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PCy$_2$) in 84% yield (486 mg). ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.02 (s, 3H, SiCH_3), 0.05 (s, 6H, SiCH_3), 0.15 (s, 6H, SiCH_3), 0.26 (s, 3H, SiCH_3), 0.70−2.38 (m, 52H, 4 C_6H_{11}, 4 PCH_2Si), 6.90−7.50 (m, 20H, NPh), 8.56 (m, 2H, TaHTa), 10.35 (m, 1H, TaHTa). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 16.28 (d, $^2J_{PP}$ = 4 Hz), 18.66 (d, $^2J_{PP}$ = 86 Hz), 149.02 (d of d, $^2J_{PP}$ = 4 Hz, 86 Hz). Anal. Calcd for $C_{60}H_{99}N_4P_3Si_4Ta_2$: C, 49.92; H, 6.91; N, 3.88. Found: C, 49.81; H, 6.67; N, 4.24.

Preparation of (^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PPh$_2$), 4a. This reaction was conducted analogously to the synthesis of **3a**. (^{PhPh}[NPN]Ta)$_2$(μ-H)$_4$ (500 mg, 0.405 mmol) and diphenylphosphine (75.41 mg, 0.405 mmol) were employed to afford (^{PhPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PPh$_2$) in 94% yield (542 mg). ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.12 (s, 3H, SiCH_3), −0.08 (s, 3H, SiCH_3), 0.01 (s, 9H, SiCH_3), 0.28 (s, 9H, SiCH_3), 0.34 (s, 3H, SiCH_3), 0.37 (s, 3H, SiCH_3), 1.13−1.45 (m, 8H, PCH_2Si), 6.48, 6.60, 6.85, 6.96, 7.10, 7.38, 7.68, 7.75, 7.80 (m, 40H, NPh, PPh, PPh$_2$) 9.31 (m, 2H, TaHTa), 10.46 (br, 1H, TaHTa). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 13.10 (d, $^2J_{PP}$ = 87 Hz), 14.05 (d, $^2J_{PP}$ = 12 Hz), 136.27 (d of d, $^2J_{PP}$ = 12 Hz, 87 Hz).

Preparation of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PPh$_2$), 4b. This reaction was conducted analogously to the synthesis of **3a**. (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$ (500. mg, 0.401 mmol) and diphenylphosphine (74.6 mg, 0.401 mmol) were employed to afford (^{CyPh}[NPN]Ta)$_2$(μ-H)$_3$(μ-PPh$_2$) in 96% yield (554 mg). ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ 0.08 (s, 9H, SiCH_3), 0.15 (s, 3H, SiCH_3), 0.21 (s, 6H, SiCH_3), 0.34 (s, 3H, SiCH_3), 0.70−1.80 (m, 30H, C_6H_{11}, PCH_2Si), 6.80, 7.00, 7.05, 7.18, 7.35, 7.52 (m, 30H, NPh, PPh), 9.15 (m, 2H, TaHTa), 10.20 (s, 1H, TaHTa). ^{31}P-{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 19.38 (d, $^2J_{PP}$ = 2 Hz), 21.41 (d, $^2J_{PP}$ = 89 Hz), 115.39 (d of d, $^2J_{PP}$ = 2 Hz, 89 Hz). Anal. Calcd for $C_{60}H_{87}N_4P_3Si_4Ta_2$: C, 50.34; H, 6.13; N, 3.91. Found: C, 50.00; H, 5.95; N, 4.24.

Preparation of (^{PhPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PCy), 5a. The following procedure is representative of the synthesis of compounds **5** and **6**. Cyclohexylphosphine (47.01 mg, 0.405

(38) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(39) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.
(40) Baudler, M.; Zarkdas, A. *Chem. Ber.* **1965**, *104*, 1034.
(41) Ohashi, A.; Matsukawa, S.; Imamoto, T. *Heterocycles* **2000**, *52*, 905.
(42) Setter, H.; Last, W. D. *Chem. Ber.* **1969**, *102*, 3364.

mmol) was added under Ar via microsyringe to a solution of (^{PhPh}[NPN]Ta)$_2$(μ-H)$_4$ (500.0 mg, 0.405 mmol) in 20 mL of Et_2O prepared in a vessel equipped with a Kontes valve. An immediate color change from purple to red was observed along with concomitant gas evolution. The solution was stirred for another 30 min to ensure complete reaction, and the solvent was removed. The resulting red solid was dissolved in pentane and then dried under vacuum to afford (^{PhPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PCy) (89%, 487 mg). ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.08 (s, 6H, SiCH_3), 0.15 (s, 6H, SiCH_3), 0.20 (s, 6H, SiCH_3), 0.22 (s, 6H, SiCH_3), 0.96−1.70 (m, 19H, C_6H_{11}, PCH_2Si), 6.82, 6.89, 7.05, 7.19, 7.25, 7.32, 7.51, 7.67 (m, 30H, NPh, PPh), 10.87 (m, 2H, Ta*H*Ta). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 10.74 (d, $^2J_{PP}$ = 152 Hz), 15.01 (d, $^2J_{PP}$ = 17 Hz), 449.0 (d of d, $^2J_{PP}$ = 17 Hz, 152 Hz).

Preparation of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PCy), 5b. This reaction was conducted analogously to the synthesis of **5a**. Cyclohexylphosphine (46.6 mg, 0.401 mmol) and (^{CyPh}[NPN]-Ta)$_2$(μ-H)$_4$ (500 mg, 0.401 mmol) were employed to afford (^{CyPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PCy) (93%, 508 mg). ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.18 (s, 6H, SiCH_3), 0.22 (s, 12H, SiCH_3), 0.23 (s, 6H, SiCH_3), 0.65−1.95 (m, 30H, C_6H_{11}, PCH_2Si), 6.85 (m, 2H, NPh), 7.14 (m, 4H, NPh), 7.30 (m, 4H, NPh), 10.47 (m, 2H, Ta*H*Ta). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 16.58 (d, $^2J_{PP}$ = 154 Hz), 22.09 (d, $^2J_{PP}$ = 18 Hz), 436.38 (d of d, $^2J_{PP}$ = 18 Hz, 154 Hz). Anal. Calcd for $C_{54}H_{87}N_4P_3Si_4Ta_2$: C, 47.71; H, 6.45; N, 4.12. Found: C, 47.44; H, 6.29; N, 4.27.

Preparation of (^{PhPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PAd), 6a. This reaction was conducted analogously to the synthesis of **5a**. Adamantylphosphine (68.1 mg, 0.405 mmol) and (^{PhPh}[NPN]-Ta)$_2$(μ-H)$_4$ (500 mg, 0.405 mmol) were employed to afford (^{PhPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PAd) (88%, 499.9 mg). ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.11 (s, 6H, SiCH_3), 0.22 (s, 12H, SiCH_3), 0.28 (s, 6H, SiCH_3) 0.95 (s, 6H, PC(CH_2)$_3$), 1.29−1.57 (m, 8H, PCH_2), 1.68 (s, 6H, CHCH_2CH), 1.75 (s, 3H, CH_2CH(CH_2)$_2$), 6.86 (m, 8H, NPh), 7.09−7.40 (m, 14H, NPh, PPh), 7.77 (m, 4H, PPh), 10.93 (m, 2H, Ta*H*Ta). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 7.35 (d, $^2J_{PP}$ = 162 Hz), 10.23 (d, $^2J_{PP}$ = 12 Hz), 474.26 (d of d, $^2J_{PP}$ = 12 Hz, 162 Hz). Anal. Calcd for $C_{58}H_{79}N_4P_3Si_4Ta_2$: C, 49.78; H, 5.69; N, 4.00. Found: C, 49.78; H, 5.49; N, 4.14.

Preparation of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PAd), 6b. This reaction was conducted analogously to the synthesis of **5a**. Adamantylphosphine (67.5 mg, 0.401 mmol) and (^{CyPh}[NPN]-Ta)$_2$(μ-H)$_4$ (500 mg, 0.401 mmol) were employed to afford (^{CyPh}[NPN]Ta)$_2$(μ-H)$_2$(μ-PAd) (97%, 549 mg). Crystals of **6b** suitable for X-ray diffraction were grown from slow evaporation of a concentrated solution of **6b** in pentane. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.11 (s, 6H, SiCH_3), 0.25 (s, 6H, SiCH_3), 0.30 (s, 6H, SiCH_3), 0.31 (s, 6H, SiCH_3) 1.08−1.88 (m, 30H, C_6H_{11}, PCH_2Si), 1.39 (s, 6H, PC(CH_2)$_3$), 1.78 (s, 6H, CHCH_2CH), 2.06 (s, 3H, CH_2CH(CH_2)$_2$), 6.87−6.91 (m, 4H, NPh), 7.15−7.23 (m, 8H, NPh), 7.29−7.36 (m, 8H, NPh), 10.61 (m, 2H, Ta*H*Ta). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 14.37 (d, $^2J_{PP}$ = 160 Hz), 19.80 (s), 468.35 (d, $^2J_{PP}$ = 160 Hz).

Preparation of (^{CyPh}[NPN]Ta)$_2$(μ-D)$_4$, d_4-1b. (^{CyPh}[NPN]-Ta)$_2$(μ-D)$_4$ is prepared analogously to **1b**, except D_2 gas is added to the diethyl ether solution of ^{CyPh}[NPN]$TaMe_3$ (1.00 g, 1.50 mmol), affording a bright purple solution after 24 h. The solvent was removed in vacuo, and the product extracted into degassed pentane and filtered through Celite. Removal of pentane affords (^{CyPh}[NPN]Ta)$_2$(μ-D)$_4$ in 94% yield (0.88 g, 0.705 mmol). The product is highly nitrogen-sensitive in solution, but is stable under nitrogen in solid form at −35 °C. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ 0.18 (s, 12H, SiCH_3), 0.24 (s, 12H, SiCH_3), 0.37−1.89 (m, 30H, C_6H_{11}, PCH_2Si), 6.95 (s, 4H, NPh), 7.17 (s, 8H, NPh), 7.35 (s, 8H, NPh). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 29.30 (s).

Preparation of (^{CyPh}[NPN]Ta)$_2$(μ-D)$_2$(μ-H)(μ-PCy$_2$), d_2-3b. A solution of (^{PhPh}[NPN]Ta)$_2$(μ-D)$_4$ (100 mg, 0.081 mmol) in degassed C_6D_6 (1 mL) was prepared in a Wilmad 5 mm NMR tube fitted with a rubber septum. To this solution, dicyclohexylphosphine (16.0 mg, 0.081 mmol) in degassed C_6D_6 (1 mL) was added via microsyringe through the septum. Mixing of the solutions promoted a color change from purple to red, and the reaction was then monitored by ^{1}H and ^{31}P NMR spectroscopy. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.21, −0.02, 0.07, 0.17, 0.23, 0.31 (s, 24H, SiCH_3's), 0.88−2.65 (m, 30H, C_6H_{11}, PCH_2Si), 6.65−7.62 (m, 30H, NPh, PPh), 8.67 (m, 0.65H, Ta*H*Ta), 10.47 (m, 0.33H, Ta*H*Ta). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 10.47 (d, $^2J_{PP}$ = 12 Hz), 10.53 (d, $^2J_{PP}$ = 83 Hz), 164.38 (d of d, $^2J_{PP}$ = 12 Hz, 83 Hz). Similar results were observed for the addition of dicyclohexylphosphine to (^{PhPh}[NPN]Ta)$_2$(μ-D)$_4$. ^{1}H NMR: δ 8.56 (m, 0.63H, Ta*H*Ta), 10.35 (m, 0.33H, Ta*H*Ta).

Details of Competition Experiment between 1b and d_4-1b. A solution of dicyclohexylphosphine (8.0 mg, 0.0405) in C_6D_6 (2 mL) was added via syringe through a rubber septum into an NMR tube containing an intimate mixture of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_4$ (50.5 mg, 0.0405 mmol), (^{CyPh}[NPN]Ta)$_2$-(μ-D)$_4$, (50.0 mg, 0.0405 mmol), and ferrocene (7.5 mg, 0.0405 mmol). The crude contents of the flask were analyzed by ^{1}H-{^{31}P} NMR spectroscopy. ^{1}H NMR: δ 8.67 (m, 1.38H, Ta*H*Ta), 10.47 (m, 0.69H, Ta*H*Ta).

Preparation of (^{CyPh}[NPN]Ta)$_2$(μ-H)$_{0.67}$(μ-D)$_{1.33}$(μ-PCy), d_x-6b. A solution of (^{CyPh}[NPN]Ta)$_2$(μ-D)$_4$ (100 mg, 0.081 mmol) in degassed C_6D_6 (1 mL) was prepared in a Wilmad 5 mm NMR tube fitted with a rubber septum. To this solution, cyclohexylphosphine (9.4 mg, 0.081 mmol) in degassed C_6D_6 (1 mL) was added via microsyringe through the septum. Mixing of the solutions promoted a color change from purple to red, and the reaction was then monitored by ^{1}H and ^{31}P NMR spectroscopy. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): δ −0.08, 0.15, 0.20, 0.22 (s, 24H, SiCH_3's), 0.96−1.70 (m, 19H, C_6H_{11}, PCH_2Si), 6.82−7.67 (m, 30H, N*Ph*, P*Ph*), 10.87 (m, 0.65H, Ta*H*Ta). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 202.5 MHz): δ 10.74 (d, $^2J_{PP}$ = 152 Hz), 15.01 (d, $^2J_{PP}$ = 17 Hz), 449.0 (d of d, $^2J_{PP}$ = 17 Hz, 152 Hz). Similar results were observed for the addition of cyclohexylphosphine to (^{PhPh}[NPN]Ta)$_2$(μ-D)$_4$. ^{1}H NMR: δ 10.47 (m, 0.69H, Ta*H*Ta).

Acknowledgment. We thank NSERC of Canada for funding (Discovery Grant to M.D.F., PGS B Scholarship to M.P.S.). M.P.S. was also supported by a Killam Predoctoral Fellowship and a Li Tse Fong Fellowship. Thanks are also extended to Mr. Christopher D. Carmichael for collection of X-ray data.

Supporting Information Available: Information on X-ray data collection and processing for **3a** and **6b**. X-ray crystallographic data for **3a** and **6b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0490076