# Bruce A. MacKay, Samuel A. Johnson, Brian O. Patrick, and Michael D. Fryzuk

**Abstract:** The reaction of the side-on, end-on ditantalum dinitrogen complex  $([NPN]Ta)_2(\mu-\eta^1:\eta^2-N_2)(\mu-H)_2$  (where NPN = PhP(CH<sub>2</sub>SiMe<sub>2</sub>NPh)<sub>2</sub>) with a variety of secondary and primary boranes is reported. With 9-BBN, hydroboration of the Ta<sub>2</sub>N<sub>2</sub> unit occurs via B-H addition, which in turn triggers a cascade of reactions that result in N—N bond cleavage, ancillary ligand rearrangement involving silicon group migration, and finally elimination of benzene from the N-Ph group and a B-H moiety to generate the imide–nitride derivative. In the presence of excess 9-BBN, the Lewis acid – base adduct of the imide–nitride ( $[NP\mu-N]Ta(=NBC_8H_{14})(\mu-NB(H)C_8H_{14})Ta[NPN]$ ) is formed. A similar set of reactions is observed for dicyclohexylborane (Cy<sub>2</sub>BH), which hydroborates the dinitrogen complex to generate [NPN]Ta(H)( $\mu$ - $\eta^1:\eta^2$ -NNBCy<sub>2</sub>)( $\mu$ -N)(Ta[NPN], followed by loss of H<sub>2</sub> and silicon group migration to yield the imide–nitride [NP $\mu$ -N]Ta(=NBCy<sub>2</sub>)( $\mu$ -N)(Ta[NPN]. With thexyl borane (H<sub>2</sub>BCMe<sub>2</sub>CHMe<sub>2</sub>), a similar sequence of reactions is suggested starting with hydroboration to generate [NPN]Ta(H)( $\mu$ - $\eta^1:\eta^2$ -NNB(H)C<sub>6</sub>H<sub>13</sub>)( $\mu$ -H)<sub>2</sub>Ta[NPN], followed by loss of H<sub>2</sub> and ancillary ligand rearrangement. When bis(pentafluorophenyl)borane (HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>) is used, no hydroboration of coordinated N<sub>2</sub> is observed, rather simple adduct formation to give ([NPN]Ta)<sub>2</sub>( $\mu$ - $\eta^1:\eta^2$ -NN-B(H)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>)( $\mu$ -H)<sub>2</sub> occurs.

Key words: dinitrogen, tantalum, hydroboration, N-N bond cleavage.

**Résumé :** On rapporte les résultats de la réaction du complexe de diazote ditantale ([NPN]Ta)<sub>2</sub>( $\mu$ -η<sup>1</sup>:η<sup>2</sup>-N<sub>2</sub>)( $\mu$ -H)<sub>2</sub> (dans lequel NPN = PhP(CH<sub>2</sub>SiMe<sub>2</sub>NPh)<sub>2</sub>) avec une variété de boranes secondaires et primaires. Avec le 9-BBN, l'hydroboration de l'unité Ta<sub>2</sub>N<sub>2</sub> se produit par une addition B-H, qui provoque à son tour une cascade de réactions conduisant à une rupture de la liaison N—N, un réarrangement du ligand impliquant une migration du groupe du silicium et finalement l'élimination du benzène du groupe N-Ph et une portion B-H pour générer la formation du dérivé imide–nitrure ([NPµ–N]Ta(=NBC<sub>8</sub>H<sub>14</sub>)( $\mu$ -NB(H)C<sub>8</sub>H<sub>14</sub>)Ta[NPN]). On observe un ensemble de réactions semblables avec le dicyclohexylborane (Cy<sub>2</sub>BH) qui provoque une hydroboration du complexe de diazote pour générer le [NPN]Ta(H)( $\mu$ -η<sup>1</sup>:η<sup>2</sup>-NNBCy<sub>2</sub>)( $\mu$ -H)<sub>2</sub>Ta[NPN], suivie d'une perte de H<sub>2</sub> et de la migration du groupe du silicium pour conduire à la formation de l'imide nitrure [NP $\mu$ -N]Ta(=NBCy<sub>2</sub>)( $\mu$ -N)Ta[NPN]. Avec le thésylborane (H<sub>2</sub>BCMe<sub>2</sub>CHMe<sub>2</sub>), la réaction suivrait un cours semblable qui débuterait avec une hydroboration pour générer le [NPN]Ta(H)( $\mu$ -η<sup>1</sup>:η<sup>2</sup>-NNB(H)C<sub>6</sub>H<sub>13</sub>)-( $\mu$ -H)<sub>2</sub>Ta[NPN], suivie d'une perte de H<sub>2</sub> et d'un réarrangement de ligand. Avec le bis(pentafluorophényl)borane (HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>), on n'observe pas l'hydroboration du N<sub>2</sub> coordiné, uniquement la formation d'un adduit simple qui génère le ([NPN]Ta)<sub>2</sub>( $\mu$ -η<sup>1</sup>:η<sup>2</sup>-NN-B(H)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>)( $\mu$ -H)<sub>2</sub>.

Mots clés : diazote, tantale, hydroboration, scission de la liaison N-N.

[Traduit par la Rédaction]

#### Introduction

The activation of small molecules by metal complexes is a mature area of inorganic chemistry. Nevertheless, molecular nitrogen, one of the most abundant small molecules in the biosphere, continues to frustrate inorganic chemists because of its intrinsic lack of reactivity (1–5). Under extreme conditions, N<sub>2</sub> will react with H<sub>2</sub> over an activated iron surface to generate ammonia; this energy-intensive catalytic transformation, known as the Haber–Bosch process, supplies the

global need for NH<sub>3</sub>-derived fertilizers (6). While discovery of a homogeneous version of the Haber–Bosch process is the goal of a number of groups around the world (7, 8), another worthwhile goal is to develop a process that converts molecular nitrogen to high-value organonitrogen materials, such as amines, substituted hydrazines, and *N*-heterocycles (9–15).

A key challenge in devising any homogeneous catalytic cycle involving molecular nitrogen is coordination of  $N_2$  to the metal centre. Because dinitrogen is intrinsically unreactive, formation of  $N_2$  complexes is not straightforward.

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Scheme 1.



Since the first report of a dinitrogen complex in 1965 (16), many N<sub>2</sub> derivatives have been synthesized (17-20). The most common method of synthesis generally requires strongly reducing conditions, which unfortunately is incompatible with many functionalization protocols. Recently, we reported (21) a facile method for the formation of a ditantalum dinitrogen complex that involves reaction of N<sub>2</sub> with the ditantalum tetrahydride 1 (Scheme 1). This reaction proceeds smoothly to generate the side-on, end-on dinitrogen complex 2 without the necessity of added reducing agents. It occurred to us that multiple additions of some simple hydride reagent (E-H) across the Ta<sub>2</sub>N<sub>2</sub> core of 2 could regenerate the starting tetrahydride 1 and produce a functionalized hydrazine moiety  $(N_2E_4)$ . Since addition of  $N_2$  to 1 reforms the dinitrogen complex 2, this could result in a catalytic sequence.

To test this hypothesis, we have examined the reaction of **2** with a number of simple hydride reagents, and preliminary communications have already been published (22, 23). In the case where E-H is 9-borabicyclo[3.3.1]nonane (9-BBN), one E-H addition occurs cleanly; however, a catalytic cycle was precluded because of an ancillary ligand dominated rearrangement. Nevertheless, this work did allow the discovery of a new type of N—N bond cleavage process that results from functionalization of coordinated N<sub>2</sub>. In this paper, we report the full details of the reaction of the dinitrogen complex **2** with some primary and secondary boranes.

#### **Results and discussion**

As summarized in Scheme 2, our initial attempt at E-H addition to 2 using 9-BBN resulted in the first example of a hydroborated dinitrogen complex (3). It was found that addition product 3 is thermally unstable and undergoes  $H_2$  elimination and N—N bond cleavage, presumably via the unobserved intermediate A, followed by silicon migration from the ancillary ligand to the bridging nitride to generate 4. We presume that the final step is elimination of benzene via the B—H bond and the phenyl of the Ta=N-Ph unit to generate the final imide-nitride 5. Postulation of this proposed scheme was facilitated by the X-ray crystal structures of intermediates 3 and 4, and final product 5, along with detailed labeling experiments (22).





# Attempted second hydroboration — Synthesis and characterization of [NPN]Ta(H)( $\mu$ -N<sub>2</sub>-B(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>)( $\mu$ -H)<sub>2</sub>Ta[NPN] (6)

Having established that hydroboration of 2 with 9-BBN leads to N-N bond cleavage and the formation of reactive nitrides, we examined multiple additions of 9-BBN to further test the catalytic plan shown in Scheme 1. Addition of 2 or more equiv. of 9-BBN to 2 resulted in a complicated mixture of products as observed by <sup>31</sup>P NMR spectroscopy. Although none of the products were immediately identifiable, there did seem to be a major product present; unfortunately, it could not be separated from the other materials present. Fortuitously, addition of 1 equiv. of 9-BBN to imide-nitride 5 resulted in the clean formation of this same major product unencumbered by impurities. This new complex 6 has two resonances (1:1 integration) in its <sup>31</sup>P NMR spectrum that are distinct from those of 5, and the <sup>1</sup>H NMR spectrum does not feature resonances indicative of tantalum hydrides. To determine its identity, crystals of 6 were obtained from a cooled THF solution and subjected to X-ray diffraction analysis.

The solid-state molecular structure of **6** (Fig. 1) shows that a simple Lewis acid – base reaction between the bridging nitride in **5** and the B atom of 9-BBN has taken place. This second equiv. of 9-BBN occupies a position roughly equal to that of the single 9-BBN fragment in intermediate **4** (Scheme 2). The N3—B2 bond length of 1.516(5) Å suggests a N—B single bond (24). The borylimido group is deflected towards the phosphine donor Pl by the presence of the second equiv. of 9-BBN. Other than this, complex **6** is very similar in structure to **5**.

In solution, the presence of the boron hydride is implied by a broad <sup>1</sup>H NMR resonance integrating to one proton at  $\delta$  4.32 ppm. In the solid state, hydrogen atom H71 was reFig. 1. ORTEP drawing of the solid-state molecular structure of 6 as determined by X-ray crystallography (ellipsoids at 50%) probability). Silvl methyls and phenyl ring carbons other than ipso are omitted for clarity. H71 was refined isotropically. Selected bond lengths (Å), bond angles (°), and torsion angles (°): Ta1-N1 1.824(3), N1-B1 1.404(5), Ta1-N2 2.175(3), N2-Ta2 1.947(3), Ta2-N3 1.854(3), N3-Ta1 2.156(3), N3-B2 1.516(5), N2-Si1 1.738(3), Ta1-N4 2.126(3), Ta1-P1 2.5825(10), Ta2-N5 2.091(3), Ta2-N6 2.048(3), Ta2-P2 2.7737(10); Ta1-N2-Ta2 93.87(11), N2-Ta2-N3 91.05(12), Ta2-N3-Ta1 97.23(13), N3-Ta1-N2 77.58(11), Ta1-N1-B1 179.3(3), Ta1-N3-B2 88.6(3), N1-Ta1-P1 86.99(10), N1-Ta1-N4 123.12(13), Ta1-N2-Si1 139.05(16), N3-Ta2-N5 101.25(13), N3-Ta2-N6 103.04(12), N3-Ta2-P2 171.01(9), Ta1-N2-Ta2-N3 3.87(11), Ta1-Ta2-N2-Si1 6.9(6), N1-Ta1-N2-Ta2 -117.54(13), P1-Ta1-Ta2-P2 13.46(4), Ta2-N2-Ta1-N4 98.92(14).



fined isotropically, and thus its position as shown in Fig. 1 is likely based on the structures obtained for 4 as well as the position and coordination geometry of B2. This reaction is shown in eq. [1]. Significantly, the intramolecular reaction to give 5 from 3 proceeds whether additional hydroboration



reagent is present or not; as mentioned above, the 2:1 reaction between 9-BBN and **2** also gives mostly **6** when this reaction is monitored by  ${}^{31}$ P NMR spectroscopy, indicating that 9-BBN is not competent to intercept the nascent nitrido intermediate postulated in the transformation of **4** to **5**, either

by hydroboration or simple Lewis acid adduct formation. This precludes hydroboration as the appropriate E-H addition to completely satisfy the proposal of Scheme 1.

#### A homologous series of complexes prepared with dicyclohexylborane (Cy<sub>2</sub>BH) and thexyl borane (H<sub>2</sub>BCMe<sub>2</sub>CHMe<sub>2</sub>)

We wondered about the generality of the cascade of reactions shown in Scheme 2. The ability to cleave coordinated  $N_2$  and to generate a new N—B bond was incentive to examine whether or not other borane reagents would engage in similar outcomes or in fact open up new reaction pathways. Given the ready availability of different organoborane reagents, this seemed worthwhile.

The reaction of 1 equiv. of dicyclohexylborane (Cy<sub>2</sub>BH) with **2** in toluene gives [NPN]Ta(H)( $\mu$ - $\eta$ <sup>1</sup>: $\eta$ <sup>2</sup>-NNBCy<sub>2</sub>)( $\mu$ -H)<sub>2</sub>Ta[NPN] (**7**) in 93% yield after stirring for 12 h (eq. [2]).



Identification of 7 was facilitated by the similarity of its <sup>1</sup>H and <sup>31</sup>P NMR spectra to those of the initial 9-BBN adduct (3). Thus, the <sup>1</sup>H NMR spectrum of 7 indicates  $C_1$  solution symmetry (eight silyl methyl resonances and two separate one-proton resonances associated with bridging hydrides are present), and a new resonance at  $\delta$  16.04 ppm implies the existence of a new terminal hydride, as was found for 3. The solid-state molecular structure of 7 was not established.

Does 7 decompose in the same manner as 3 (Scheme 2)? Toluene or THF solutions of 7 show conversion to [NPµ- $NTa(=NPh)(\mu-NB(H)Cy_2)Ta[NPN]$  (8) in similar yield and on a time scale comparable to the decomposition of 3 into 4. Therefore, hydroboration and N-N bond cleavage are both possible using Cy<sub>2</sub>BH interchangeably with 9-BBN. The solid-state molecular structure of 8 has been determined and it is shown in Fig. 2. The relative orientations of the phenylimido ligand and H85 are similar to 4. The fact that N-N bond scission and silvl group migration from an [NPN] ligand amide to the new dinitrogen-derived nitrido ligand have occurred in an exactly analogous fashion is evident. Bond lengths and angles are comparable to those of 4, except that the [NPN] ancillary ligand bound to Ta2 of complex 8 is rotated by  $70^{\circ}$  about the Ta-Ta axis as compared to its position in 4.

Like its 9-BBN analogue 4, 8 is observed via NMR spectroscopy to eliminate benzene in  $d^8$ -THF solution, and at the

**Fig. 2.** ORTEP drawing (spheroids at 50% probability) of **8** ([NP $\mu$ -N]Ta(=NPh)( $\mu$ -NB(H)Cy<sub>2</sub>)Ta[NPN]). Silyl methyl and phenyl ring carbons other than ipso omitted for clarity. H85 was located in the electron difference map and refined isotropically. Selected bond lengths (Å), bond angles (°), and torsion angles (°): Ta1—N1 2.142(3), Ta1—N2 2.191(3), Ta1—N3 1.788(3), Ta1—N4 2.146(3), Ta1—P1 2.6370(11), N1—B1 1.532(7), B1—H1 1.59(6), Ta1—H1 1.90(8), N2—Si1 1.738(3), N1—N2 2.675(3), Ta2—N5 2.070(3), Ta2—N6 2.066(3), Ta2—P2 2.7897(10); N1-Ta1-N2 76.31(12), Ta1-N2-Ta2 94.88(12), N2-Ta2-N1 90.40(13), Ta2-N1-Ta1 98.41(13), Ta1-N1-B1 89.8(2), N1-B1-H1 190.2(6), N1-Ta1-N3 117.17(13), N1-Ta1-N4 114.08(11), N1-Ta1-P1 136.84(8), N1-Ta2-N5 114.35(12), N1-Ta2-N6 117.00(13), N1-Ta2-P2 99.46(9), Ta1-N2-Ta2-N1 0.25(11), P1-Ta1-Ta2-P2 –143.96(4), N1-Ta1-N2-Si1 -176.8(2), N2-Ta1-N1-B1 -169.8(2).



same time, <sup>31</sup>P NMR resonances of a new species (9) arise. Identification of this complex as ([NPµ-N]Ta(=NBCy<sub>2</sub>)(µ-N)Ta[NPN] was made by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy in analogy to that already shown in Scheme 2. This new imide-nitride 9 forms cleanly from 8 in an overall yield of 83% as measured by <sup>31</sup>P NMR spectroscopy against an internal reference. This is an improvement over the conversion of 4 to 5, in which many other <sup>31</sup>P NMR-active sideproducts were detected. Although the change from 9-BBN to dicyclohexylborane does not significantly attenuate hydroboration of 1 or N-N bond cleavage, it did increase the yield of 9 vs. the yield of 5. In Scheme 3, this chemistry is summarized starting with hydroboration adduct 7; loss of H<sub>2</sub> triggers N—N bond cleavage, presumably through an unobserved intermediate such as **B**, which then undergoes silicon migration from the ancillary [NPN] ligand to generate 8 and finally 9 via loss of benzene. Presumably, addition of another equivalent of dicyclohexylborane to 9 would produce an adduct similar to 6 in eq. [1]; however, this was not pursued.

Since hydroboration of **2** and N—N bond cleavage occurred for the secondary boranes 9-BBN and  $Cy_2BH$ , it was of interest to examine the course of the reactions with a priScheme 3.



mary borane. The presence of another boron hydride for intramolecular reactions after an initial hydroboration suggested the possibility of different post-hydroboration reaction paths including another potential opportunity to form N—H bonds. The 1:1 reaction between **2** and thexyl borane (H<sub>2</sub>BCMe<sub>2</sub>CHMe<sub>2</sub>) proceeds to completion over 12 h as shown in eq. [3] to give [NPN]Ta(H)( $\mu$ - $\eta$ <sup>1</sup>: $\eta$ <sup>2</sup>-NNB(H)C<sub>6</sub>H<sub>13</sub>)( $\mu$ -H)<sub>2</sub>Ta[NPN] (**10**) in 92% yield.



Although crystals suitable for X-ray diffraction were not isolated, the <sup>1</sup>H NMR spectrum of **10** shows the expected  $C_1$  symmetry and the new resonance characteristic of a terminal hydride at  $\delta$  15.52 ppm, analogous to that already observed for **3** and **7**. The remaining boron hydride is evident as a broad singlet at  $\delta$  4.42 ppm that integrates to one proton.

As for complexes **3** and **7**, solutions of **10** are thermally unstable. The rearranged product (**11**) has no resonances suggestive of bridging or terminal hydride ligands in its <sup>1</sup>H NMR spectrum, and the <sup>31</sup>P NMR resonances of **11** do not unequivocally make it a sister complex to **4** or **8**. The <sup>1</sup>H NMR spectrum is indicative of  $C_1$  symmetry, and the resonances can be assigned as [NPµ-N]Ta(=NPh)(µ-NB(H)<sub>2</sub>C<sub>6</sub>H<sub>13</sub>)Ta[NPN], as shown in eq. [4].



Satisfactory elemental analysis was obtained for this formulation, but the solid-state molecular structure of 11 has not been established. The only indication that **11** might be other than that suggested is that it does not degrade via elimination of benzene to a congener of 5 or 9. Instead it can be observed by <sup>31</sup>P NMR spectroscopy to convert into a number of different products over a week. None of these were spectrally related to 5 or 9. Hydroboration of 2 with thexyl borane may lead to new rearrangements for 8 that were not observed with secondary boranes, but characterization of the resulting complexes has not been possible. It is likely that the additional B-H functionality coupled with the already documented propensity for ancillary ligand rearrangements in this system renders this combination too reactive. With group 6 dinitrogen complexes, the reaction with the yl borane results in a totally different and distinct outcome than described herein (25) (Table 1).

# Synthesis of $([NPN]Ta)_2(\mu-\eta^1:\eta^2-NN-B(H)(C_6F_5)_2)(\mu-H)_2$ (12)

Although the dinitrogen unit of **2** can be derivatized by hydroboration, it is not clear how to remove the functionalized dinitrogen moiety or the dinitrogen-derived atoms in the descendant complexes from the bimetallic core, because the Ta–N interactions remain quite strong. It was postulated that a more Lewis acidic borane might react in a similar manner to 9-BBN, but would remove additional electron density from the dinitrogen moiety, and thus greatly weaken the Ta–N bonds. A straightforward synthesis of the strongly Lewis acidic secondary borane HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> has recently been reported (26, 27), and so the reactivity of this borane with **2** was investigated.

The reaction of HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> with complex **2** occurs immediately; however, the colour of the solution changes from the red-brown of **2** to a dark yellow-brown colour, rather than to an orange colour as observed for the B-H addition adducts **3**, **7**, and **10**. Two new resonances are observed in the <sup>31</sup>P NMR spectrum at  $\delta$  10.0 and  $\delta$  22.8 with a  $J_{PP}$  value of 25.1 Hz. A broad peak at  $\delta$  4.7 in the <sup>1</sup>H NMR spectrum integrates to a single proton. The location and broadness of this resonance identifies it as a hydrogen atom bound to boron. A similar peak is observed in the <sup>1</sup>H NMR spectrum of the starting borane HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>. The <sup>15</sup>N NMR spectrum of the <sup>15</sup>N<sub>2</sub>enriched complex <sup>15</sup>N<sub>2</sub>-**12**, which was prepared by the reaction of <sup>15</sup>N<sub>2</sub>-**2** with HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, contains two resonances, at  $\delta$  -46.9 and  $\delta$  24.0. The resonance at  $\delta$  -46.9 is a doublet of doublets, with a <sup>2</sup>J<sub>NP</sub> value of 25.9 Hz and a <sup>1</sup>J<sub>NN</sub> value of 15.3 Hz. As for <sup>15</sup>N<sub>2</sub>-**2**, the chemical shift of this resonance and the large coupling to <sup>31</sup>P indicates that this is the end-on

nitrogen. The chemical shift of the second <sup>15</sup>N resonance ( $\delta = 24.0$ ) is much closer to that observed in the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct of <sup>15</sup>N<sub>2</sub>-2 ( $\delta$  2.4) than to <sup>15</sup>N<sub>2</sub>-3 ( $\delta$  –114.8), where a tantalum hydride bond is formed. This reaction product is, therefore, not related to complexes 3, 7, and 10, which are the products of B-H addition. Rather, this spectral information indicates that 12 is more closely related to the Lewis acid – base adducts of 2 with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, GaMe<sub>3</sub>, and AlMe<sub>3</sub>, (28) and can be assigned as [NPN]Ta( $\mu$ - $\eta$ <sup>1</sup>: $\eta$ <sup>2</sup>-NN-B(H)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>)( $\mu$ -H)<sub>2</sub>Ta[NPN]. As for these complexes and parent complex 2, the solution symmetry of 12 is C<sub>s</sub> as evidenced by the four unique silyl methyl resonances in its <sup>1</sup>H NMR spectrum. The formation of complex 12 is illustrated in eq. [5].



This assignment was confirmed by X-ray crystallography. An ORTEP drawing of the solid-state molecular structure of **12** is shown in Fig. 3. Hydrides were not located in the diffraction experiment, but the  $Ta_2N_2$  core bonding and the relative disposition of the ancillary [NPN] ligands is reminiscent of parent complex **2** and of its Lewis acid adducts.

Upon hydroboration, the N—N bond was elongated from 1.319(4) Å in 2 to 1.411(15) Å in 3. The same bond in 12 is only marginally elongated as compared to the starting dinitrogen complex and the other metric parameters of the Ta<sub>2</sub>N<sub>2</sub> core are similar. Therefore, derivatizaton of the coordinated N<sub>2</sub> unit of 2 with strongly Lewis acidic boranes does not affect core bonding. Like 2 and its Lewis adducts, 12 is a stable molecule as compared to 3, 7, and 10, and it shows no propensity to undergo the reductive elimination and N—N bond scission common to these complexes. It seems that addition of the H—B bond across the exposed Ta=N bond of 2 is a precondition for these processes. The theoretically predicted reversal of the polarity of this bond in HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> vs. dialkylboranes may preclude this reaction, implying that E—H bond polarity is a important consideration in selecting

	$[NP\mu-N]Ta(=N-BC_8H_{14})(\mu-N-B(H)C_8H_{14})Ta[NPN]$ (6)	$[NP\mu-N]Ta(=NPh)(\mu-N-B(H)(C_{6}H_{11})_{2})Ta[NPN] (8)$	([NPN]Ta) <sub>2</sub> (µ-NN- B(H)(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> )(µ-H) <sub>2</sub> ( <b>11</b> )
CCDC registry	250128	250129	250130
Formula	C <sub>58</sub> H <sub>86</sub> N <sub>6</sub> P <sub>2</sub> Ta <sub>2</sub> Si <sub>4</sub> B <sub>2</sub> [C <sub>6</sub> H <sub>6</sub> ]	$C_{67}H_{93}N_6Ta_2P_2Si_4B$	$C_{60}H_{65}BF_{10}N_6P_2Si_4Ta_2(C_6H_6)_{2.5}$
FW	1581.39	1518.70	1802.46
Colour, habit	Yellow, chip	Yellow, chip	Dark, block
Crystal dimensions (mm)	$0.20 \times 0.15 \times 0.15$	$0.35 \times 0.20 \times 0.10$	$0.32 \times 0.24 \times 0.16$
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P\overline{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	11.7634(4)	12.0875(4)	17.2272(3)
<i>b</i> (Å)	25.6823(8)	13.7220(4)	24.5044(2)
c (Å)	24.0178(9)	20.9574(8)	18.4711(3)
α (°)	90	91.266(3)	90
β (°)	96.180(2)	90.784(3)	95.071(1)
γ (°)	90	84.952(3)	90
V (Å <sup>3</sup> )	7213.9(4)	3461.5(2)	7766.9(2)
Ζ	4	2	4
$\rho_{calcd}$ (g/cm <sup>3</sup> )	1.46	1.46	1.54
<i>F</i> (000)	3208.00	1538.00	3596.00
$\mu$ (MoK $\alpha$ ) (mm <sup>-1</sup> )	3.181	3.312	2.988
Transmission factors	0.6368-1.0000	0.7278-1.0000	0.8192-1.0000
2θ <sub>max</sub> (°)	55.8	55.7	56.0
Total no. of reflns.	62 376	31 854	46 043
No. of unique reflns.	16 351	14 230	15 345
R <sub>merge</sub>	0.053	0.062	0.043
No. reflns with $I \ge n \sigma(I)$	12735 (n = 2)	11 678 $(n = 2)$	$15\ 345\ (n=2)$
No. of variables	775	720	881
$R$ ( $F^2$ , all data)	0.043	0.039	0.036
$R_w$ ( $F^2$ , all data)	0.068	0.074	0.076
$R (F, I > n\sigma(I))$	0.029	0.029	0.046
$R_w$ (F, I > $n\sigma(I)$ )	0.062	0.071	0.081
GOF	0.94	0.098	1.088

**Table 1.** X-ray crystallographic information for complexes 6, 8, and 11.<sup>3</sup>

**Note:** Rigaku/ADSC CCD diffractometer,  $R = \sum ||F_0^2| - |F_c^2|| / \sum |F_0^2|$ ;  $R_w = (\sum w (|F_0^2| - |F_c^2|)^2 / \sum w |F_0^2|^2)^{1/2}$ .

reagents for any scheme bent on using 2 for catalytic functionalization of  $N_2$ .

# Summary

The initial study of the hydroboration of a dinuclear tantalum dinitrogen complex with 9-BBN has been extended to other monoalkyl- and dialkylboranes. In all cases, the N<sub>2</sub> complexes, derivatized by H—B bond addition across the exposed Ta=N bond, spontaneously undergo reductive elimination of two bridging hydrides as H<sub>2</sub> coupled to N—N bond cleavage without loss of the new B—N bond. This cascade of reactions is only somewhat attenuated by different substituents on the hydroboration reagent. Subsequent addition reactions across new Ta=N moieties do not occur, but the additional equivalents of hydroboration reagent can be incorporated into the complex as alkylborohydride adducts. Bis(pentafluorophenyl)borane HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> fails to react with the starting dinitrogen complex 2 in the same manner as the alkylboranes; instead, a stable adduct is formed, likely a result of the enhanced Lewis acidity of the boron centre owing to the presence of the perfluorophenyl substituents. This is summarized in Scheme 4.

# **Experimental section**

### **General considerations**

Unless otherwise stated, all manipulations were performed under an atmosphere of dry oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system and a -60 °C freezer). Anhydrous hexanes and toluene were purchased from Aldrich, sparged with dinitrogen, and passed through columns containing activated alumina and Ridox catalyst before use. Anhydrous diethylether was stored over sieves and distilled from so-

<sup>&</sup>lt;sup>3</sup>Supplementary data may be purchased from the Directory of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub\_e.shtml for information on ordering electronically). CCDC 250128–250130 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via ww.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

**Fig. 3.** ORTEP depiction of the solid-state molecular structure of  $([NPN]Ta)_2(\mu-\eta^1:\eta^2-NN-B(H)(C_6F_5)_2)(\mu-H)_2$  (**12**) as determined by X-ray crystallography. The bridging hydrides and the hydrogen bound to boron were not located. The silyl methyl groups and fluorine atoms are omitted for clarity, and only the ipso carbons of the PPh and NPh groups are shown. Selected bond lengths (Å) and bond angles (°): N5—N6 1.368(4), Ta1—Ta2 2.8903(2), Ta1—N5 2.186(3), Ta1—N6 1.964(3), Ta2—N5 1.878(3), N6—B1 1.557(5), Ta1—P1 2.6089(10), Ta2—P2 2.6265(10); Ta1-N5-Ta2 90.36(12), Ta1-N6-N5 79.8(2), Ta1-N6-B1 155.6(3).



dium benzophenone ketyl under argon. Pentane was stored over sieves and distilled from sodium benzophenone ketyl solublized by tetraglyme under dry dinitrogen prior to storage over a potassium mirror. Tetrahydrofuran was heated at reflux over  $CaH_2$  prior to distillation from sodium benzophenone ketyl under argon. 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. Deuterated tetrahydrofuran and toluene were dried by refluxing with molten potassium metal in a sealed vessel under vacuum, then trap-to-trap-distilled, and freeze–pump–thaw degassed three times. Unless otherwise stated, <sup>1</sup>H, <sup>31</sup>P, <sup>1</sup>H{<sup>31</sup>P}, <sup>13</sup>C, <sup>11</sup>B, <sup>15</sup>N, <sup>29</sup>Si-DEPT, and two-dimensional NMR spectra were recorded on either a Bruker AMX-500 instrument (5 mm BBI probe) operating at 500.1 MHz for <sup>1</sup>H or a Bruker AVA-400 instrument (5 mm BBI probe) operating at 400.1 MHz for <sup>1</sup>H. <sup>1</sup>H NMR spectra were referenced to residual proton in deuterated solvent as follows: C<sub>4</sub>D<sub>7</sub>HO ( $\delta$  3.58 ppm), C<sub>6</sub>D<sub>5</sub>H ( $\delta$  7.15 ppm), and

Scheme 4.



 $C_7D_7H$  (δ 2.09 ppm). <sup>31</sup>P NMR spectra were referenced to external P(OMe)<sub>3</sub> (δ 141.0 ppm with respect to 85% H<sub>3</sub>PO<sub>4</sub> at δ 0.0 ppm) or internal P(OMe)<sub>3</sub> flame-sealed inside a 1 mm × 25 mm glass capillary tube if required, <sup>13</sup>C NMR spectra to <sup>13</sup>CC<sub>5</sub>D<sub>6</sub> (δ 128.4 ppm) and <sup>13</sup>CD<sub>2</sub>Cl<sub>2</sub> (δ 54.0 ppm), <sup>11</sup>B spectra to neat BF<sub>3</sub>·Et<sub>2</sub>O (δ 0.0 ppm), <sup>15</sup>N spectra to external nitromethane at 0.0 ppm, and <sup>29</sup>Si to Me<sub>4</sub>Si 50% in CDCl<sub>3</sub> (δ 0.0 ppm). Elemental analyses were performed by Mr. P. Borda and Mr. M. Lakha, of The University of British Columbia Department of Chemistry.

The syntheses of complexes **1**, **2** (21), **3**, **4**, and **5** (22), dicyclohexylborane (29), thexyl borane (30), and  $HB(C_6F_5)_2$  (27) were performed as described in the literature.

### $[NP\mu-N]Ta(=N-BC_8H_{14})(\mu-NB(H)C_8H_{14})Ta[NPN] (6)$

To a stirred 15 mL toluene solution of 5 (298 mg, 0.229 mmol) was added dropwise 0.25 mL (1.1 equiv.) of 1.0 mol/L 9-BBN solution in THF. The resulting mixture was stirred overnight and the <sup>31</sup>P NMR spectrum of a small portion indicated that the reaction had proceeded to consume all of complex 5, giving exclusively resonances of 6. After evaporation of solvent and precipitation from pentane, 241 mg (0.169 mmol, 74% yield) of 6 was recovered on a frit. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, 400 MHz) δ: -0.69, -0.21, 0.05, 0.13, 0.25, 0.34, 0.43, (s, 3H each) SiCH<sub>3</sub>; 0.84, 0.97 (d, 1H each)  $PCH_2$ , complicated overlapping multipets from 0.70 to 2.26 (total 39H), B-C<sub>8</sub> $H_{14}$  and PC $H_2$  (solvent was contaminated with a small amount of hexanes) 4.32 (b, 1H), B-H; 6.73, 6.79, 6.81, 6.85, 6.93, 7.07, 7.09, 7.20 (s, d, t, some peaks obscured by solvent) C<sub>6</sub>H<sub>5</sub>-N and C<sub>6</sub>H<sub>5</sub>-P; (7.51 (d, 2H,  $J_{\rm HH}$  = 6.95 Hz), 7.94 (d, 2H,  $J_{\rm HH}$  = 7.05 Hz), o-C<sub>6</sub>H<sub>5</sub>-P. <sup>31</sup>P NMR ( $C_6D_6$ , 300 K, 161.9 MHz) & -12.52 (b), 27.26 (s). Anal. calcd. for C<sub>58</sub>H<sub>86</sub>B<sub>2</sub>N<sub>6</sub>P<sub>2</sub>Si<sub>4</sub>Ta<sub>2</sub>: C 48.88, H 6.08, N 5.90; found: C 49.12, H 6.23, N 5.81.

# [NPN]Ta(H)( $\mu$ - $\eta$ <sup>1</sup>: $\eta$ <sup>2</sup>-NNBCy<sub>2</sub>)( $\mu$ -H)<sub>2</sub>Ta[NPN](7)

Toluene (25 mL) was added to an intimate mixture of dry 2 (0.412 g, 0.327 mmol) and white solid dicyclohexylborane (58.2 mg, 1 equiv.) in a glove box. The resulting mixture was stirred vigorously overnight, the solvent was evaporated, and the residues were triturated under hexanes, giving 0.438 mg (0.305 mmol, 93.2% yield) of **7**. <sup>1</sup>H NMR (500.1 MHz,  $C_6D_6$ , 300 K)  $\delta$ : -0.37, -0.22, -0.17, -0.05, -0.10, -0.01, 0.09, 0.14 (s, 24H total), SiCH<sub>3</sub>; 0.28, 0.40, 0.64, 0.73, 0.77, 0.86, 1.09, 1.15 to 1.34 (broad), 1.47, 1.59,

and 1.77 (broad overlapping resonances), cyclohexyl and PCH<sub>2</sub>; 6.61, 6.66, 6.73, 6.82, 6.88, 6.96, 7.13 to 7.26 (overlapping), 7.29, 7.38, and 7.70 (overlapping doublets, triplets, 20H total, some resonances obscured by solvent) P-C<sub>6</sub>H<sub>5</sub> and N-C<sub>6</sub>H<sub>5</sub>; 8.14 (d,  $J_{PH} = 6.38$  Hz), 8.24 (d,  $J_{PH} = 6.82$  Hz), *o*-P-C<sub>6</sub>H<sub>5</sub>; 10.70 and 11.51 (d, 1H each,  $J_{HH} = 10.0$  Hz)  $\mu$ -H; 16.04 (d,  $J_{PH} = 14.6$  Hz), Ta-H. <sup>13</sup>C NMR was not recorded. <sup>31</sup>P NMR (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K)  $\delta$ : 7.98 (d,  $J_{PP} = 10.2$  Hz), 20.0 (d,  $J_{PP} = 10.2$  Hz). Anal. calcd. for C<sub>60</sub>H<sub>87</sub>BN<sub>6</sub>P<sub>2</sub>Si<sub>4</sub>Ta<sub>2</sub>: C 50.07, H 6.09, N 5.84; found: C 50.35, H 6.34, N 5.48.

# Decomposition of 7 to [NPµ-N]Ta(=NPh)(µ-NB(H)Cy<sub>2</sub>)Ta[NPN] (8)

A capped THF solution of 396 mg (0.275 mmol) 7 was left in a glove box at ambient temperature for 3 weeks and then cooled in a -60 °C freezer, giving crystals of 8. Yield 0.186 g, 0.129 mmol, 47%. <sup>1</sup>H NMR (400.1 MHz, C<sub>7</sub>D<sub>8</sub>, 300 K) & -1.13, -0.90, -0.09, -0.15, -0.36, 0.18, 0.34 (s, 24H total), SiCH<sub>3</sub>; 0.50, 1.16 (d, 1H each) PCH<sub>2</sub>; -0.01, 0.68, 0.87, 1.06, 1.33, 1.45, 1.48 (broad overlapping multiplets, total 26H) B-C<sub>6</sub> $H_{11}$  and PC $H_2$ ; 4.09 (b, FWHM 32 Hz, 1H) BH; 6.28, 6.30, 6.34, 6.40, 6.50, 6.74, 6.83, 6.94, 7.00, 7.11, 7.18 (overlapping doublets, triplets, 20H total, some resonances obscured by solvent)  $P-C_6H_5$  and N- $C_6H_5$ ; 7.84 (d,  $J_{PH} = 6.59$  Hz), 7.49 (d,  $J_{PH} = 7.06$  Hz), (10H total) o-P-C<sub>6</sub> $H_5$ . <sup>13</sup>C NMR (100.6 MHz, C<sub>7</sub>D<sub>8</sub>, 300 K)  $\delta$ : -1.77, -0.80, -0.64, 0.30, 2.67, 2.75, 3.30, 5.39, SiCH<sub>3</sub>; 32.85 (b), B-C<sub>ipso</sub> of cyclohexyl; 11.14, 15.45, 18.19, 25.93, 26.05, CH<sub>2</sub> of cyclohexyl; 20.99, 25.32, 26.05, 26.41, 27.16, 29.99, 30.49, 31.58, P-CH<sub>2</sub>; 118.27, 119.03, 120.98, 122.79, 123.16, 123.29, 125.70, 126.98, 127.15, 127.51, 127.74, 128.56, 133.56, 135.84 (some resonances obscured by solvent),  $P-C_6H_5$  and  $N-C_6H_5$ ; 127.62, 131.96,  $o-P-C_6H_5$ ; 151.24, 158.19, ipso-P-C<sub>6</sub>H<sub>5</sub>. <sup>31</sup>P NMR (161.9 MHz, C<sub>7</sub>D<sub>8</sub>, 300 K)  $\delta$ : -2.30 (d,  $J_{PP}$  = 3.1 Hz), 28.30 (d,  $J_{PP}$  = 3.1 Hz). Anal. calcd. for C<sub>60</sub>H<sub>85</sub>BN<sub>6</sub>P<sub>2</sub>Si<sub>4</sub>Ta<sub>2</sub>: C 50.14, H 5.96, N 5.85; found: C 50.28, H 6.13, N 5.46.

# Decomposition of 8 to [NPµ-N]Ta(=NBCy<sub>2</sub>)(µ-N)Ta[NPN] (9)

A  $d^8$ -THF solution of **8** suitable for NMR spectroscopy in a Wilmad NMR tube capped with a plastic stopper and sealed with ParaFilm laboratory film and bearing a sealed capillary containing internal standard was left in a glove box for 3 weeks. Spectra were acquired intermittently. After this time, the <sup>31</sup>P and <sup>1</sup>H NMR spectra were exclusively that of 8, and the integration with respect to internal standard allowed evaluation of 83% yield. The total integration of other <sup>31</sup>P NMR active resonances was 6%. <sup>1</sup>H NMR (400.1 MHz, C<sub>7</sub>D<sub>8</sub>, 300 K) δ: -1.10, -0.88, -0.34, -0.13, -0.02, 0.18, 0.20, 0.33 (s, 3H each), SiCH<sub>3</sub>; 0.49, 0.75, 0.89, 1.17, 1.21, 1.31, 1.55 (d, 1H each), P-CH<sub>2</sub>; 0.6-1.6 (complicated overlapping multiplets, 22H total), B-( $C_6H_{11}$ )<sub>2</sub>; 3.81 (b, FWHM 28 Hz, 1H) B-H; 6.27, 6.34, 6.51, 6.57, 6.63, 6.67, 6.77, 6.83, 6.86, 6.95, 6.99, 7.03, 7.11, 7.16, 7.42, 7.57 (d, t, overlapping, 26H total)  $P-C_6H_5$  and  $N-C_6H_5$ ; 7.47, 7.83 (d, 2H each), o-P- $C_6H_5$ . <sup>31</sup>P NMR (161.9 MHz,  $C_7D_8$ , 300 K)  $\delta$ : 0.76 (d,  $J_{PP}$  = 5.94 Hz), 17.41 (d,  $J_{PP}$  = 5.94 Hz). Elemental analysis was not obtained.

#### $[NPN]Ta(H)(\mu-\eta^{1}:\eta^{2}-NNB(H)C_{6}H_{13})(\mu-H)_{2}Ta[NPN] (10)$

To a stirred toluene solution of 1 (0.336 g, 0.266 mmol) was added 0.54 mL (0.27 mmol, 1.02 equiv.) of freshly prepared thexyl borane (0.5 mol/L in THF). After stirring overnight the solvents were evaporated, leaving an orange residue that was triturated under hexanes and recovered on a frit, giving 0.332 g (0.244 mmol, 91.8% yield) of solid pale orange 10. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 300 K)  $\delta$ : -0.32, -0.14, -0.05, 0.11, 0.17, 0.19, 0.25, 0.34 (s, 3H each), SiCH<sub>3</sub>; 1.21, 1.41, 1.45, 1.59, 1.61, 1.67, 1.78, 1.81 (d, 1H each) PCH<sub>2</sub>; 0.82, 0.89 (d, 3H each) 1.11, 1.23 (s, 3H each), B-C(CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>; 1.64 (m, <sup>1</sup>H) B-C(CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>; 4.42 (b, <sup>1</sup>H) B-*H*; 5.96, 6.07, 6.22, 6.28, 6.35, 6.66, 6.91, 6.94, 7.01, 7.12, 7.20, 7.22, 7.25 (d, t, total 26H), P-C<sub>6</sub>H<sub>5</sub> and N-C<sub>6</sub>H<sub>5</sub>; 7.71, 7.92 (d, 2H each) o-P-C<sub>6</sub>H<sub>5</sub>; 10.2, 11.6 (d, <sup>1</sup>H each) Ta $\mu$ H; 15.52 (s, <sup>1</sup>H) TaH. <sup>31</sup>P NMR (161.9 MHz,  $C_6H_6$ , 300 K)  $\delta$ : 8.73 (d,  $J_{PP}$  = 15.3 Hz), 24.16 (d,  $J_{PP} = 15.3$  Hz). Anal. calcd. for  $C_{54}H_{79}BN_6P_2Si_4Ta_2$ : C 47.72, H 5.86, N 6.18; found: C 47.32, H 6.26, N 6.12.

#### $[NP\mu-N]Ta(=NPh)(\mu-NB(H)_2C_6H_{13})Ta[NPN] (11)$

A 15 mL toluene solution of 0.328 g (0.241 mmol) 11 was allowed to stand in a glove box at ambient temperature for 8 days. The <sup>31</sup>P NMR spectrum of a portion of this solution showed no remaining 10, and solvent was evaporated. Solid 11 (134 mg, 41% yield) was recovered on a frit after trituration under hexanes. <sup>1</sup>H NMR (400 MHz,  $C_4D_8O_7$ ) 300 K) δ: -0.48, -0.43, -0.08, -0.02, 0.08, 0.11, 0.27, 0.34 (s, 3 H each, 24H total), SiCH<sub>3</sub>; 0.55, 0.78, 1.20, 1.30, 1.57, 1.81, 2.22, 2.36 (d, 1H each), PCH<sub>2</sub>; 0.73, 0.81, 1.40, 1.57 (s, 3H each), B-C(CH<sub>3</sub>)<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>; 3.58, 4.32 (b, 1H each), B-H; 6.76, 6.80, 6.96, 7.02, 7.05, 7.06, 7.09, 7.12, 7.14, 7.16, 7.19, 7.30, 7.33 (d, t, 1 and 2H each, 26H total) P- $C_6H_5$  and N- $C_6H_5$ ; 7.61, 8.02 (d, 2H each) P- $C_6H_5$ . <sup>31</sup>P NMR (161.9 MHz, C<sub>4</sub>D<sub>8</sub>O, 300 K) δ: -6.68 (b), 18.55 (s). Anal. calcd. for C<sub>54</sub>H<sub>77</sub>BN<sub>6</sub>P<sub>2</sub>Si<sub>4</sub>Ta<sub>2</sub>: C 47.79, H 5.72, N 6.19; found: C 47.42, H 6.10, N 6.38.

### $([NPN]Ta)_2(\mu-\eta^1:\eta^2-NNB(H)(C_6F_5)_2)(\mu-H)_2$ (12)

To a solution of 2 (0.7589 g, 0.6017 mmol) in 10 mL of C<sub>6</sub>H<sub>6</sub> was added solid HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (0.2081 g, 0.6017 mmol, 1.0 equiv.). The solution was allowed to stir for 3 h, and the product was then allowed to crystallize by slow evaporation. and collected yield The solid was dried, to  $([(NPN]_2TaH)_2N_2(HB(C_6F_5)_2)$  as a brown solid (0.943 g, 97%). <sup>1</sup>H NMR (500 MHz, C<sub>7</sub>D<sub>8</sub>, 350 K) δ: -0.28, -0.07, -0.03, 0.03 (s, 24H total, SiCH<sub>3</sub>), 0.61, 1.45, 1.68, 2.03 (AMX, 8H total,  $CH_2$  ring), 4.7 (br,  $W_{1/2} = 250$  Hz, 1H, BH), 6.77, 6.87, 6.94, 6.98, 7.06, and 7.20 (overlapping m, 26 H, NPh and PPh), 7.02 and 7.57 (m, 4H total, PPh o-H), 11.56 (dd,  ${}^{2}J_{\text{HP}} = 20.9$  Hz,  ${}^{2}J_{\text{HP}} = 17.3$  Hz, 2H, TaH). <sup>1</sup>H NMR (500 MHz, C<sub>7</sub>D<sub>8</sub>, 245 K) δ: -0.26, -0.26, -0.24, -0.17, 0.00, 0.09, 0.11, 0.41 (s, 24H total, SiCH<sub>3</sub>), 0.63, 1.05, 1.20, 1.28, 1.36, 1.39, 1.67, 2.73 (AMX, 8H total, CH<sub>2</sub>) ring), 4.7 (br, 1H, BH), 5.80, 6.16, 6.51, 6.75, 6.85 (m, 1H each, NPh or PPh) 6.91-7.37 (overlapping m, 18 H, NPh and PPh), 7.49 (m, 2H, PPh-o-H), 7.53 (m, 2H, PPh or NPh), 7.88 (m, 2H, PPh-*o*-*H*), 11.00 (br m,  ${}^{2}J_{\text{HH}} = 14.2$  Hz, 1H, Ta*H*), 11.67 (ddd,  ${}^{2}J_{\text{HH}} = 14.2$  Hz,  ${}^{2}J_{\text{HP}} = 14.7$  Hz,  ${}^{2}J_{\text{HP}} = 31.9$  Hz, 1H, Ta*H*).  ${}^{31}$ P NMR (C<sub>7</sub>D<sub>8</sub>, 299 K) & 10.0 (d,  ${}^{2}J_{\text{PP}} = 25.1$ , [NPN] ligand), 22.8 (d,  ${}^{2}J_{\text{PP}} = 25.1$ , [NPN] ligand). Anal. calcd. for  $C_{60}H_{65}BF_{10}N_6P_2Si_4Ta_2$ : C 44.84, H 4.08, N 5.23; found: C 44.77, H 4.13, N 5.10.

# $([NPN]Ta)_2(\mu-\eta^1:\eta^2-15N^{15}NB(H)(C_6F_5)_2)(\mu-H)_2$ (15N<sub>2</sub>-12)

The <sup>15</sup>N-labeled analogue was prepared in a manner identical to that used for **12**, except for using the <sup>15</sup>N-labeled precursor <sup>15</sup>N<sub>2</sub>-2. <sup>31</sup>P NMR (C<sub>7</sub>D<sub>8</sub>, 299 K) & 10.0 (dd,  $J_{PP} = 25.1$  Hz, <sup>2</sup> $J_{PN} = 17.2$  Hz, [NPN] ligand), 22.8 (d,  $J_{PP} = 25.1$  Hz, [NPN] ligand). <sup>15</sup>N NMR (C<sub>7</sub>D<sub>8</sub>, 299 K) & -48.1 (dd, <sup>1</sup> $J_{NN} = 16.2$  Hz, <sup>2</sup> $J_{NP} = 25.1$  Hz), 11.5 (d, <sup>1</sup> $J_{NN} = 16.2$  Hz).

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