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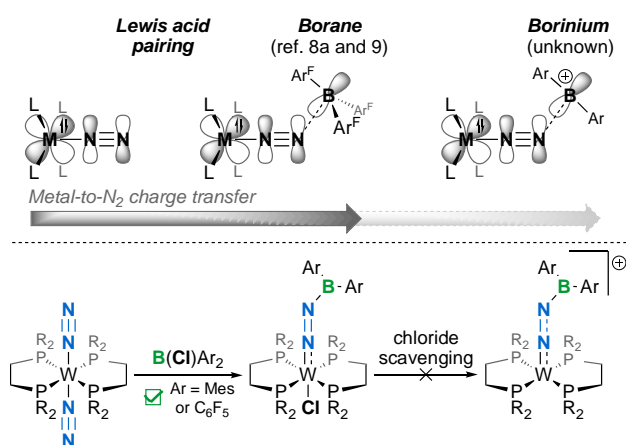
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# Dinitrogen-derived (diarylboryl)diazenido Complexes with Differing Coordination to the Thallium Cation<sup>†</sup>

Amal Bouammali, Anaïs Coffinet, Laure Vendier and Antoine Simonneau\*

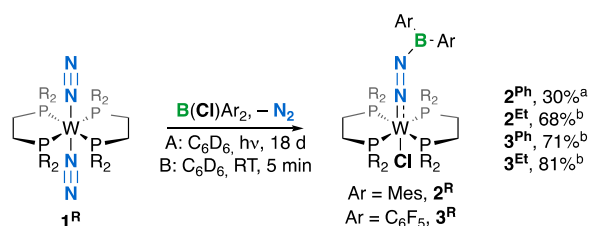
To prepare N<sub>2</sub>-derived cationic boryldiazenido-tungsten complexes as models of semimetallic metal-borinium frustrated Lewis pairs activating N<sub>2</sub>, we have attempted halide abstraction from *trans*-(diarylboryl)diazenido-halo-tungsten complexes. Reactions with Tl<sup>+</sup> led to adducts in which coordination of the cation differs depending on the boryldiazenido substituents and the ancillary ligand. Chloride scavenging was not observed.

Since their advent in the mid 1960s,<sup>1</sup> N<sub>2</sub>-complexes<sup>2</sup> have been shown to undergo a wealth of transformations, allowing chemists to build bonds between the N<sub>2</sub> ligand and several other elements.<sup>3</sup> These discoveries have culminated in the development of homogeneous catalysts for the reduction of N<sub>2</sub> into ammonia,<sup>4</sup> now considered as conceivable alternatives<sup>5</sup> to the energy- and fossil fuel-intensive Haber-Bosch process.<sup>6</sup> Our group has recently reported on dinitrogen borylation<sup>7</sup> methods employing highly Lewis acidic boranes.<sup>8</sup> We have shown these electrophilic molecules can interact with end-on bound dinitrogen ligand,<sup>8a,9</sup> affording hetero-dinuclear, N<sub>2</sub>-bridged edifices that can also be viewed as frustrated Lewis pair<sup>10</sup> templates for N<sub>2</sub> activation<sup>11</sup> (Scheme 1). Willing to exacerbate the “push-pull” effect<sup>12</sup> in these FLP templates to disclose new reactivity for the N<sub>2</sub> ligand, we have looked for a way to prepare N<sub>2</sub>-derived cationic boryldiazenido tungsten complexes as equivalent of a “M(O)-N<sub>2</sub>-borinium” dinuclear system.<sup>13</sup> Since, to the best of our knowledge, only a handful of borinium cations have been reported and they are not easily prepared,<sup>14</sup> we have first elected a route starting with the 1,3-addition of the B–Cl bond of a diarylchloroborane over the M–N<sub>2</sub> unit of Hidai-Chatt tungsten complexes.<sup>15</sup> This synthesis would give *trans*-(diarylboryl)diazenido chloro complexes and would offer variability for the boron substituents. Subsequently, chloride scavenging using BAr<sup>F</sup><sub>4</sub> salts (Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) would afford the targeted cationic (diarylboryl)diazenido complexes (Scheme 1). This last step failed, but we could isolate and characterize Tl adducts of the boryldiazenido complexes, structurally contrasting by the basic site binding the Tl atom. This points to a possible differentiation regarding the interaction of N<sub>2</sub>-derived complexes with electrophiles that must be considered in the context of homogeneously catalysed nitrogen fixation.<sup>4,15c,16</sup>



**Scheme 1** Boron Lewis acid-enhanced N<sub>2</sub> activation through a push-pull mechanism: expected increased charge transfer upon borinium coordination (top) and envisioned synthetic strategy to access W–N<sub>2</sub>-borinium adducts (bottom).

According to our strategy, we have treated the tungsten complexes *trans*-[W(dppe)<sub>2</sub>(N<sub>2</sub>)<sub>2</sub>] (**1<sup>Ph</sup>**) and *trans*-[W(depe)<sub>2</sub>(N<sub>2</sub>)<sub>2</sub>] (**1<sup>Et</sup>**) (dppe: 1,2-bis(diphenylphosphino)ethane; depe: 1,2-bis(diethylphosphino)ethane) with two different diarylchloroboranes, namely B(Cl)Mes<sub>2</sub> (Mes = mesityl or 2,4,6-trimethylphenyl) and B(Cl)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (Scheme 2). Small-scale reactions in a sealable NMR tube in C<sub>6</sub>D<sub>6</sub> at room-temperature were almost instantaneous, with high spectroscopic yields of the boryldiazenido complexes **2<sup>Et</sup>** and **3<sup>R</sup>** according to <sup>31</sup>P NMR. A notable exception was when we reacted B(Cl)Mes<sub>2</sub> with **1<sup>Ph</sup>**, since no evidence of B–N bond formation could be recorded even upon heating. However, under irradiation (365 nm), the boryldiazenido compound **2<sup>Ph</sup>** slowly formed. A ~40% conversion was recorded according to <sup>31</sup>P NMR monitoring after 18 days.



**Scheme 2** Synthesis of boryldiazenido(chloro)tungsten complexes. <sup>a</sup> Conditions A. <sup>b</sup> Conditions B.

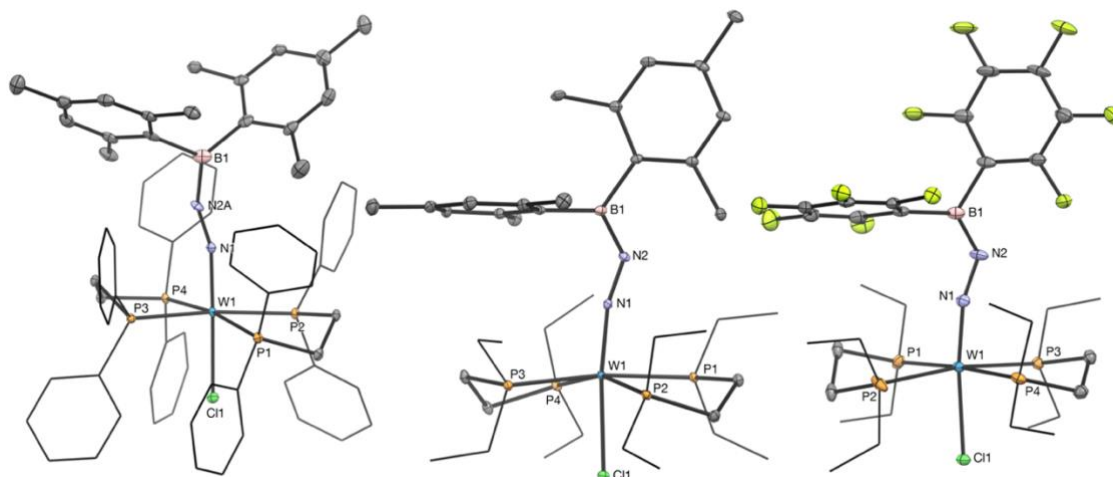
Single crystals of **2<sup>Ph</sup>**, **2<sup>Et</sup>** and **3<sup>Et</sup>** suitable for an X-ray diffraction analysis could be grown, confirming the formal 1,3-addition of the B–Cl bond (Fig. 1).<sup>‡</sup> Selected metrical parameters for the solid-state structures are reported in Table 1. Slight differences appear by comparison of the data, but overall the structures are rather similar. The W–N bond shortens in the series **2<sup>Ph</sup>** > **2<sup>Et</sup>** > **3<sup>Et</sup>**, a trend that reverses when considering the N–N bond

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<sup>†</sup> Electronic Supplementary Information (ESI) available: detailed experimental procedures, NMR and FTIR spectra, and crystallographic data. CCDC 2114361–2114366 and 2122445.

length. Those parameters can be linked to the charge transfer from the metal to the N<sub>2</sub> unit. Its amplitude varies depending on the  $\sigma$ -donation of the supporting ligand (depe > dppe, cf. **2<sup>Ph</sup>** vs. **2<sup>Et</sup>**) and the electron-withdrawing ability of the boryl group (B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> > BMes<sub>2</sub>, cf. **2<sup>Et</sup>** vs. **3<sup>Et</sup>**). The N-N distances are longer than two times the double-bond covalent radius of nitrogen,<sup>17</sup> pointing to a bond order less than 2. The W-N distances (ca. 1.8 Å) are consistent with W-N double bonding. Collectively, these data are in agreement with the assignment of a +II formal oxidation state for the tungsten centre, which is also supported by the diamagnetism of the complexes. The 3 structures display a W-N-N array that deviates from linearity (ca. 165°). This is probably the result of steric repulsion between the aryl

substituents of the boron atom and the substituents of the phosphines. The N-N-B angles are close to 130° for **2<sup>Et</sup>** and **3<sup>Et</sup>**, but significantly wider for **2<sup>Ph</sup>** (155°). They remain within the range (from 129° up to 178°)<sup>8,15a,b</sup> of values found in other structurally characterized W(II) boryldiazenido complexes, with higher ones being recorded when bulky substituents are present on both the boron atom and the metal's ligands.<sup>15a,b</sup> The tungsten centre adopts a distorted octahedral geometry as a result of diphosphines' small bite angle and the difference of steric hindrance of the two apical ligands, the phosphines being pushed towards the chloride (average of N-W-P angles > 93°).



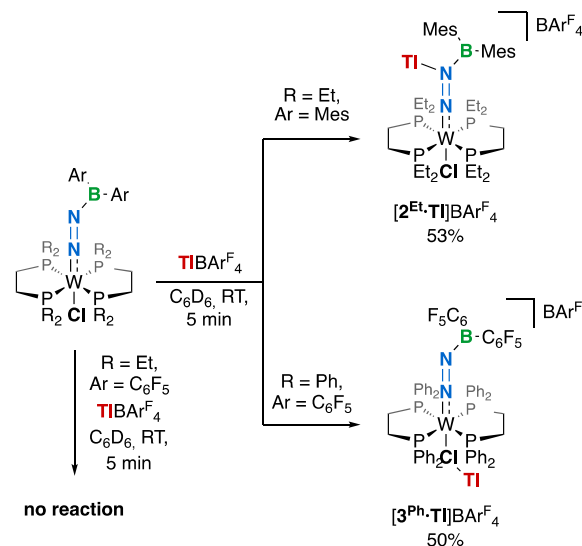
**Fig. 1** Solid-state molecular structures of compounds **2<sup>Ph</sup>** (left), **2<sup>Et</sup>** (middle) and **3<sup>Et</sup>** (right), with ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted and phenyl or ethyl substituents are depicted as wireframes for clarity.

**Table 1** Selected bond lengths and angles for compounds **2<sup>Ph</sup>**, **2<sup>Et</sup>** and **3<sup>Et</sup>** in the solid-state.

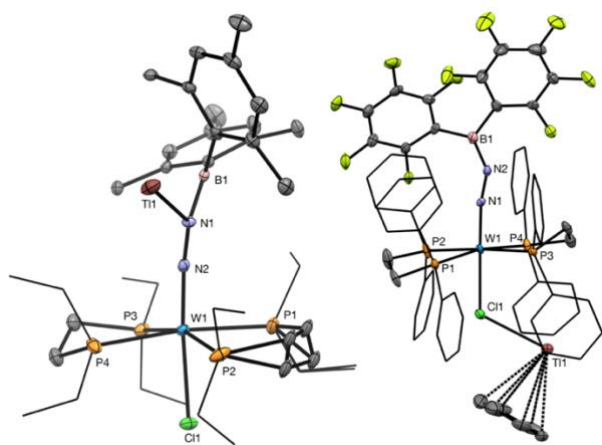
Distance (Å)/Angle (°)	<b>2<sup>Ph</sup></b>	<b>2<sup>Et</sup></b>	<b>3<sup>Et</sup></b>
W-N	1.842(3)	1.802(2)	1.781(3)
N-N	1.25(2)	1.276(3)	1.298(4)
N-B	1.40(2)	1.409(4)	1.374(5)
W-N-N	163.1(7)	166.0(2)	164.2(3)
N-N-B	155(1)	132.8(2)	129.0(3)

We then attempted to remove the chloride from the metal centre using different chloride abstractors. However, our tests employing either NaBARF<sub>4</sub> or AgBARF<sub>4</sub> in various solvents have not been conclusive: large signals and baseline thickening were observed upon monitoring of the reaction by NMR, suggesting the presence of paramagnetic species. Indeed, in the case of **3<sup>Et</sup>**, we could collect low amounts of brown-yellow crystals of [WCl<sub>2</sub>(depe)<sub>2</sub>]BARF<sub>4</sub> (not shown, see Fig. S38). The fact that some redox chemistry takes place in the presence of a sodium salt intimates that cationic boryldiazenido complexes may exhibit uncontrolled redox chemistry. Contrastingly, selective reactions occurred for **2<sup>Et</sup>** and **3<sup>Ph</sup>** in the presence of TIBARF<sub>4</sub> in C<sub>6</sub>D<sub>6</sub> or C<sub>6</sub>D<sub>5</sub>Cl, according to <sup>1</sup>H and <sup>31</sup>P NMR. However, **3<sup>Et</sup>** remained basically unchanged (Scheme 3).<sup>9</sup> The new compounds crystallized out of the reaction medium in moderate yields, and the obtained material could be submitted to an X-ray diffraction analysis. The solid-states structures revealed that TI adducts

**2<sup>Et</sup>·TI<sup>+</sup>** and **3<sup>Ph</sup>·TI<sup>+</sup>** formed, the tungsten centres retaining their chloride ligand (Fig. 2).



**Scheme 3** Reactivity of the tungsten-chloro-boryldiazenido complexes with the thallium(I) cation.



**Fig. 2** Solid-state molecular structures of compounds  $2^{\text{Et}}\cdot\text{Tl}^+$  (left) and  $3^{\text{Ph}}\cdot\text{Tl}^+$  (right), with ellipsoids drawn at the 30% probability level. Hydrogen atoms and counter-ion have been omitted and ethyl or phenyl substituents are depicted as wireframes for clarity.

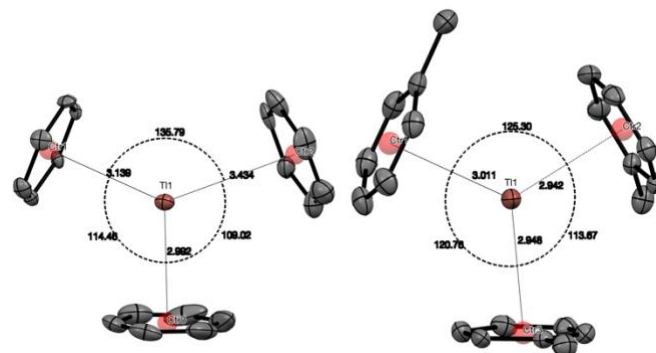
**Table 2** Selected bond lengths and angles for compounds  $2^{\text{Et}}\cdot\text{Tl}^+$  and  $3^{\text{Ph}}\cdot\text{Tl}^+$  in the solid-state.

Distance (Å)/Angle (°)	$2^{\text{Et}}\cdot\text{Tl}^+$	$3^{\text{Ph}}\cdot\text{Tl}^+$
W-N	1.780(6)	1.803(7)
N-N	1.315(9)	1.25(1)
N-B	1.420(8)	1.37(1)
W-Cl	2.524(2)	2.500(2)
N-Tl	2.622(7)	n.a.
Cl-Tl	n.a.	2.930(2)
W-N-N	166.3(5)	169.1(6)
N-N-B	128.4(5)	142.2(8)
N-N-Tl	131.8(4)	n.a.
W-Cl-Tl	n.a.	117.72(8)

Selected bond lengths and angles concerning these two structures are compiled in Table 2. Comparing the structures of  $2^{\text{Et}}$  and  $2^{\text{Et}}\cdot\text{Tl}^+$  is relevant here. In the latter, the thallium cation binds the terminal nitrogen of the boryldiazene ligand, and short contacts are found in the unit cell with a mesityl C atom, and a chloride and a fluoride of neighbouring molecules. The main differences with  $2^{\text{Et}}$  are a shortened W–N and elongated N–N bonds, as a result of augmented  $\pi$  back-donation from the metal centre induced by coordination of the  $\text{Tl}^+$  Lewis acid. The basic site the cation binds differs radically in the two molecules. In  $3^{\text{Ph}}\cdot\text{Tl}^+$ ,  $\text{Tl}^+$  binds the trans chloride ligand. This outcome is somewhat counter-intuitive as we have previously noticed the high Lewis basicity of boryldiazene bound to tungsten, even when they feature the electron-withdrawing group  $\text{B}(\text{C}_6\text{F}_5)$ .<sup>8c</sup> The solution  $^1\text{H}$  NMR spectrum of  $3^{\text{Ph}}\cdot\text{Tl}^+$  in  $\text{C}_6\text{D}_6$  is also rather intriguing as it is characteristic of a highly symmetric molecule, the ethylenic and aromatic protons being undifferentiated, by contrast with  $3^{\text{Ph}}$ . Our assumption is that  $\text{Tl}^+$  coordination may not be “fixed” in solution, resulting in an averaged spectrum at room temperature. Unfortunately, variable temperature NMR experiments in  $\text{C}_6\text{D}_6$  or toluene- $d_8$  were plagued by crystallization of  $3^{\text{Ph}}\cdot\text{Tl}^+$ , but the  $^1\text{H}$  spectrum in  $\text{PhCl}-d_5$  exhibits clearly differentiated resonances for the aromatic and ethylenic protons (see Fig. S27–28).

$\text{Tl}^+$  is a soft cation known to form arene complexes,<sup>18</sup> and inter- and intra-molecular short contacts are found between a

benzene molecule present in the unit cell and the two closest Ph rings of the dppe ligand (Fig. 2, right, and Fig. 3, left), comparing well with the structure of  $[\text{Tl}(\text{toluene})_3]^+$ .<sup>18h</sup> Like in the latter compound (Fig. 3, right), the Tl atom in  $3^{\text{Ph}}\cdot\text{Tl}^+$  lies in the plane formed by the 3 Ph centroids, although more pronounced irregularities are found for the angles of the trigonal planar arrangement. The distances to the centroids of the Ph rings belonging to the dppe ligand are rather long, Tl⋯Ar distances being usually found between 2.9 and 3.1 Å. These deviations are likely due to the constrained placement of thallium’s Ph and Cl ligands in  $3^{\text{Ph}}\cdot\text{Tl}^+$ . The weak interaction with dppe’s Ph rings may also be explained by the  $\text{P}\rightarrow\text{W}$  substituent deactivating the arene, as well as partial quenching of thallium’s charge due to chloride binding.



**Fig. 3** Comparison of the  $\text{Tl}^+\cdots\text{arene}$  arrangement found in the structure of  $3^{\text{Ph}}\cdot\text{Tl}^+$  (left) and the one of  $[\text{Tl}(\text{toluene})_3]^+$  (right).<sup>54</sup> Distances are given in Å, angles in °.

## Conclusions

We have attempted the synthesis of cationic boryldiazenido-tungsten complexes to judge the impact of  $\text{N}_2$  “push-pull” activation in “W(0)-borinium” FLP templates, benchmarking against the already reported  $\text{B}(\text{C}_6\text{F}_5)_3$  adducts.<sup>8a,19</sup> We could prepare and fully characterize boryldiazenido(chloro)-tungsten complexes by formal 1,3 addition of the B–Cl bond of diaryl chloroboranes, a reaction that complements the one reported by Braunschweig and employing aryl dichloroboranes.<sup>15b</sup> However, chloride scavenging with Na or Ag  $\text{BAr}^{\text{F}_4}$  seemed to be accompanied with undesired redox processes. Thallium salts contrastingly led to well-defined species, but not resulting from chloride abstraction. The soft  $\text{Tl}^+$  cation instead binds either the terminal nitrogen of the boryldiazene ligand in  $2^{\text{Et}}\cdot\text{Tl}^+$ , or the trans chloride ligand in  $3^{\text{Ph}}\cdot\text{Tl}^+$ , binding that seems to be favoured through stabilizing interactions with a molecule of solvent (benzene) and two phenyl rings of the dppe ligand. Future work will focus on the direct generation of cationic boryldiazenido-tungsten complexes from W(0)- $\text{N}_2$  complexes and borinium cations.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

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## Notes and references

‡ Despite several attempts, crystal structure resolution for **3<sup>Ph</sup>** were systematically problematic. A low resolution one can be found in the ESI (Fig. S36).

§ Given the low yield of **2<sup>Ph</sup>**, we have not attempted Cl scavenging on this compound.

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