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## COMMUNICATION

## Paddlewheel 1,2,4-Diazaphospholide Dibismuthanes with Very Short Bismuth–Bismuth Single Bonds

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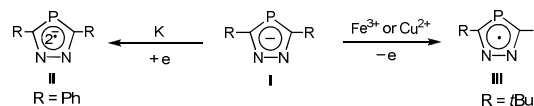
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**One-electron oxidation of the 1,2,4-diazaphospholide anion [3,5-R<sub>2</sub>dp]<sup>−</sup> by BiCl<sub>3</sub> generated several remarkable paddlewheel dibismuthanes [L<sub>2</sub>(Bi–Bi)L<sub>2</sub>] (L = η<sup>1</sup>,η<sup>1</sup>-3,5-R<sub>2</sub>dp, R = *t*Bu, *i*Pr, or Ph) with very short Bi–Bi single bond lengths (2.7964(4)–2.8873(3) Å).**

Bismuth complexes containing bismuth–transition metal or bismuth–bismuth bonds have attracted an increasing interest during the last two decades.<sup>1,2</sup> A number of dibismuthanes containing Bi–Bi single bonds and several dibismuthenes with Bi=Bi double bonds have been prepared.<sup>2</sup> A typical dibismuthane has two pyramidal diorganobismuth moieties linked through a Bi–Bi single bond that is usually ca. 3.0 Å (the covalent radii are 3.04 Å).<sup>3</sup> The bond lengths varied very little when the Bi has different substituents.<sup>4</sup> However, the prepared dibismuthenes RBi=BiR have the Bi=Bi double bond distances of ca. 2.82 Å, about 6% shorter than the Bi–Bi single bond in dibismuthanes.<sup>5</sup> This contraction is thought to be due mainly to a π-bond formed by side-on overlap of p-orbitals on the Bi atoms.<sup>5</sup> With only few exceptions, however, the Bi–Bi bonds in the “naked” [Bi<sub>2</sub>]<sup>2−</sup> units or in a *cis*-dibismuthene, supported by samarium-,<sup>6a</sup> potassium-metal moiety<sup>6b</sup> or coordinated by two bridging “side-on” W(CO)<sub>5</sub> fragments,<sup>6c</sup> have the short Bi–Bi bond distances of 2.851(1),<sup>6a</sup> 2.8377 Å<sup>6b</sup> or the longer Bi=Bi bond distance of 3.003(1) Å,<sup>6c</sup> respectively. Another remarkable formal bismuth(II) complex, dibismuth(trifluoroacetate)<sub>4</sub>,<sup>7</sup> is currently the only known p-block paddlewheel complex. This complex has a short Bi–Bi single bond,

of 2.95 Å. The non-solvated crystalline form of the complex contains two crystallographically independent dinuclear tetrabridged [Bi<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>] units and totally lacks axial interactions of any kind between dibismuth units. This unusual complex showed the unique electronic structure and bonding characteristic in comparison to those in d-block paddlewheel complexes<sup>8</sup> and has been found to be a precursor for several novel heterodimetallic complexes<sup>9a–d</sup> that were efficient catalysts in organic transformations.<sup>9e</sup> [Bi<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>]<sup>7</sup> can be prepared by a reduction of bismuth(III) trifluoroacetate with bismuth or zinc metal at high temperature but curiously there is no any other p-block paddlewheel complex to be reported so far.

We recently introduced a family of 3,5-di-substituents-1,2,4-diazaphospholide anions ([3,5-R<sub>2</sub>dp]<sup>−</sup>, R = H, *t*Bu, *i*Pr, or Ph)<sup>10</sup> which can be used as monoanionic bidentate ligands to stabilize a number of metal ions to allow the related 1,2,4-diazaphospholide-based complexes to be prepared.<sup>11</sup> We demonstrated that these anionic ligands are non-innocent and redox-active, and that they can be reduced by metallic potassium or oxidized by hypervalent metal ions such as Fe<sup>3+</sup> and Cu<sup>2+</sup> (Scheme 1).<sup>12</sup> These results suggested that the 1,2,4-diazaphospholide ligands could support low-valent p-block metal species. The inert-s-pair or relativistic effects are expected to favor the lower oxidation states of Bi,<sup>2</sup> so we became interested in exploring low-valent Bi complex bearing the 1,2,4-diazaphospholide ligands. We found that the low-valent bismuth species could be generated by reducing readily accessible Bi(III) species directly with 1,2,4-diazaphospholide anions. Here, we describe the one-electron reduction of BiCl<sub>3</sub> by the [3,5-R<sub>2</sub>dp]<sup>−</sup> anion to give several homoleptic paddlewheel 1,2,4-diazaphospholide dibismuthanes with very short Bi–Bi single bond lengths (even shorter than the Bi=Bi double bonds that have been previously reported<sup>5</sup>). These complexes are rare examples of p-block paddlewheel complexes containing Bi–Bi bonds.



**Scheme 1.** The non-innocent 1,2,4-diazaphospholide ligands.

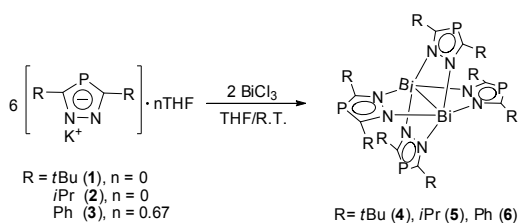
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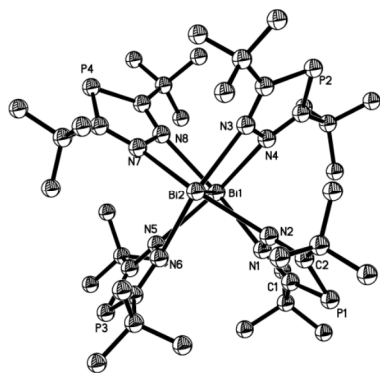
† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

The reaction between  $\text{BiCl}_3$  and  $\text{K}[3,5\text{-R}_2\text{dp}]$  ( $\text{R} = t\text{Bu}$  (**1**),<sup>11a</sup> *i*Pr (**2**),<sup>13,14</sup> or Ph (**3**)<sup>11a</sup>), at a ratio of 1:3, in tetrahydrofuran (THF) resulted in a solution with deep-color (orange red). The solution was worked up, and dibismuthane  $[\{\eta^1, \eta^1\text{-}3,5\text{-R}_2\text{dp}\}_2(\text{Bi-Bi})\{\eta^1, \eta^1\text{-}3,5\text{-R}_2\text{dp}\}_2]$  ( $\text{R} = t\text{Bu}$  (**4**), *i*Pr (**5**), or Ph (**6**)) was readily isolated as orange-red crystals in a fair yield (50.8% for **4**, 46.1% for **5**, and 40.2% for **6**) (Scheme 2). Concentrating the mother liquor allowed an additional portion of the dibismuthane to be isolated and the related colorless free ligand  $\text{H}[3,5\text{-R}_2\text{dp}]$  ( $\text{R} = t\text{Bu}$  (**7**),<sup>15</sup> *i*Pr (**8**),<sup>13</sup> or Ph (**9**)<sup>16</sup>) to be isolated in low yield (15.9% for **7**, 6.0% for **8**, and 14.9% for **9**).<sup>13</sup> The dibismuthanes **4**, **5**, and **6** were soluble in common organic solvents and decomposed at 210°C, 219°C, and 215°C, respectively.<sup>17</sup>



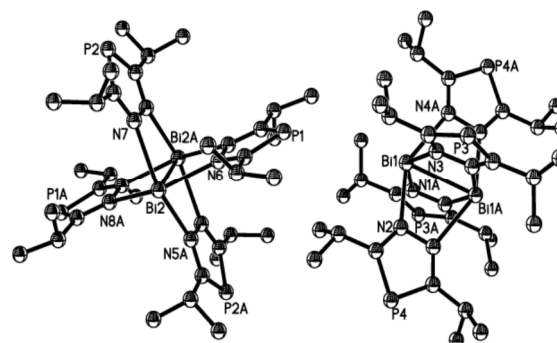
**Scheme 2.** Preparation of the paddlewheel dibismuthanes **4**, **5**, and **6**.

The elemental analysis results agreed completely with the formulae of dibismuthanes **4**, **5**, and **6**.<sup>17</sup> The  $^1\text{H}$  NMR (600 MHz,  $\text{THF-}d_8$  or  $\text{C}_6\text{D}_6$ , 23°C) spectrum of **4** showed two sets of sharp peaks, at  $\delta = 1.25$  and 1.39 ppm (72 H; the integral ratio = 1:2), for the *t*Bu groups in  $\text{THF-}d_8$ , but only one resonance in  $\text{C}_6\text{D}_6$ . The former is presumably attributable to the formation of THF-solvated adduct with **4** or to the indication of dissociation in the solution. Only one sharp and intense resonance was observed in  $^{31}\text{P}\{\text{H}\}$  NMR (243 MHz,  $\text{THF-}d_8$  or  $\text{C}_6\text{D}_6$  for **4**,  $\text{THF-}d_8$  for **6**, and  $\text{C}_6\text{D}_6$  for **5**, 23°C) spectrum of each product, at  $\delta = +79.1$  ppm for **4** (+80.20 in  $\text{C}_6\text{D}_6$ ), +61.4 for **5**, and +67.2 ppm for **6**. This peak is shifted up- or downfield relative to the corresponding signal for the free heterocyclic ligand **7**, at  $\delta = +65.4$  ppm,<sup>15</sup> **8**, at  $\delta = +66.9$ ,<sup>13</sup> and **9**, at  $\delta = +74.3$  ppm<sup>16</sup> and to the potassium salt **1**, at  $\delta = +50.6$  ppm,<sup>11a</sup> **2**, at  $\delta = +46.3$ ,<sup>14</sup> and **3**, +67.3 ppm.<sup>11a</sup> This clearly suggests that **4**, **5**, and **6** had uniform coordination environment.<sup>17</sup>



**Figure 1.** X-ray crystal structure of **4**. Drawn with ellipsoids at 30% probability and hydrogen atoms omitted for clarity. Selected bond distances [ $\text{\AA}$ ] and angles (deg).  $\text{Bi1-Bi2}$  2.7964(4),  $\text{Bi1-N1}$  2.472(7),  $\text{Bi1-N8}$  2.500(6);  $\text{N1-Bi1-N5}$  83.4(2),  $\text{N1-Bi1-Bi2}$  71.80(14).

The X-ray diffraction analysis confirmed that the dibismuthane assembly  $[\{\eta^1, \eta^1\text{-}3,5\text{-R}_2\text{dp}\}_2(\text{Bi-Bi})\{\eta^1, \eta^1\text{-}3,5\text{-R}_2\text{dp}\}_2]$  ( $\text{R} = t\text{Bu}$  (**4**), *i*Pr (**5**), or Ph (**6**)) crystallized in the monoclinic space group  $P2_1/c$  for **4** and triclinic space group  $P-1$  for **5** and **6** (Figures 1–3).<sup>17,18,19</sup> Complex **5** possessed two distinct but similar  $\text{Bi}_2$  molecules (**5a**, **5b**). As can be seen from Figures 1–3, the inversion center was at the midpoint of the Bi–Bi bond in each dibismuthane **5a**, **5b**, and **6** (but not for **4** due to twisted conformation). This indicated that the overall ligand arrangement around the  $\text{Bi}_2$  core was an almost perfect paddlewheel structure for **5a**, **5b**, and **6** but a twisted structure (because of steric substituent repulsion) for **4**. A total absence of axial interactions of any kind between the dibismuth units in **4–6** was found. Each bismuth atom was coordinated with one other Bi atom and four N atoms with a slightly distorted square pyramidal geometry. The length of the Bi–N bonds within each of **4**, **5a**, **5b** and **6** varied slightly, by ca. 0.015  $\text{\AA}$  around the average. The average Bi–N bond distance was ca. 2.484(6)  $\text{\AA}$  for **4**, 2.451(5)  $\text{\AA}$  for **5a**, 2.459(5) for **5b**, and 2.446(3)  $\text{\AA}$  for **6**. These Bi–N bond lengths are significantly shorter than those found for  $[\text{L}_2\text{Bi-BiL}_2]$  ( $\text{L} = 1\text{-phenyl-5-thiotetrazolyl anion}$ ) (2.657(4)  $\text{\AA}$ ),<sup>20</sup>  $[(2\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4)_2\text{Bi-Bi}(2\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4)_2]$  (3.027(4)  $\text{\AA}$ ),<sup>21</sup> and  $[\{1,8\text{-}(\text{NSiMe}_3)_2\text{C}_{10}\text{H}_6\}\text{Bi}]_2$  (3.0197(2)  $\text{\AA}$ ).<sup>22</sup> The Bi–Bi distance (2.7964(4)  $\text{\AA}$  in **4**, 2.8630(4)  $\text{\AA}$  in **5a**, 2.8611(4)  $\text{\AA}$  in **5b**, and 2.8873(3)  $\text{\AA}$  in **6**) were much shorter than that found in  $[\text{Bi}_2(\text{O}_2\text{CCF}_3)_4]\cdot\text{C}_6\text{Me}_6$

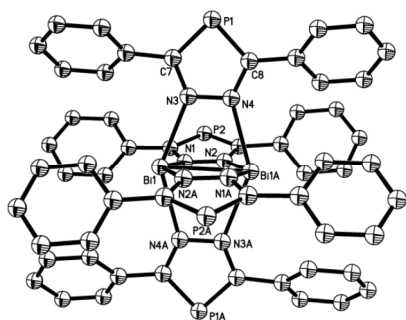


**Figure 2.** X-ray crystal structures of **5a**, **5b**. Drawn with ellipsoids at 30% probability and hydrogen atoms omitted for clarity. Selected bond distances [ $\text{\AA}$ ] and angles (deg). **5a**:  $\text{Bi1-Bi1A}$  2.8630(4),  $\text{Bi1-N2}$  2.378(5),  $\text{Bi1-N4A}$  2.522(5);  $\text{N2-Bi1-N3}$  84.17(16),  $\text{N3-Bi1-Bi1A}$  74.82(11). **5b**:  $\text{Bi2-Bi2A}$  2.8611(4),  $\text{Bi2-N5A}$  2.398(5),  $\text{Bi2-N7}$  2.517(5);  $\text{N6-Bi2-N7}$  86.16(16),  $\text{N6-Bi2-Bi2A}$  73.89(10).

(2.947(1)  $\text{\AA}$ )<sup>7a</sup> and other dibismuthanes.<sup>4</sup> Strikingly, the Bi–Bi bond in **4** was very short, even shorter than the Bi=Bi double bonds of ca. 2.82  $\text{\AA}$ .<sup>5</sup> The planes of the 1,2,4-diazaphospholide in the face-to-face orientation were almost perpendicular to each other, with an average dihedral angle of close to 90° despite the average N–Bi–N angle being 84.4(2)° in **4**, 84.8(2) in **5a** and **5b**, and 84.4(1) in **6**.

The reaction between  $\text{BiCl}_3$  and **1** (or **2/3**) is unusual, and it appears that 1,2,4-diazaphospholides are redox-active when dissolved in THF. In previous work, we demonstrated that one-electron oxidation of **1** by  $\text{FeCl}_3$  or  $\text{CuCl}_2$  occurred in toluene, giving a neutral radical  $[3,5\text{-}t\text{Bu}_2\text{dp}]^\bullet$  (by EPR) that self-associated to give a N–P coupling 1,2,4-diazaphospholyl dimer  $[\text{N},\text{P}\text{-}t\text{Bu}_2\text{dp}]_2$  (**10**) (which was fully characterized) rather than the expected homoleptic complex  $\text{Fe}[3,5\text{-}t\text{Bu}_2\text{dp}]_3$  or  $\text{Cu}[3,5\text{-}t\text{Bu}_2\text{dp}]_2$ .<sup>12b</sup> However, an attempt to isolate the corresponding low-valent metal complex, such as  $\text{Fe}[3,5\text{-}t\text{Bu}_2\text{dp}]_2$  or  $\text{Cu}[3,5\text{-}t\text{Bu}_2\text{dp}]$ , was not successful.<sup>12b</sup> Both low valent dibismuthanes and the related free ligands **7–9** were isolated from the systems when the reaction between  $\text{BiCl}_3$

and **1** (or **2** or **3**) was performed. It was therefore possible that the one-electron oxidation of **1** (or **2** or **3**) produced the neutral radical  $[3,5-R_2dp]^{\bullet}$  ( $R = tBu, iPr, \text{ or } Ph$ ) that spontaneously abstracted a hydrogen from a THF molecule to give the corresponding free ligand  $H[3,5-R_2dp]$ .<sup>23</sup>



**Figure 3.** X-ray crystal structure of **6**. Drawn with ellipsoids at 30% probability and hydrogen atoms omitted for clarity. Selected bond distances ( $\text{\AA}$ ) and angles (deg). Bi1–Bi1A 2.8873(3), Bi1–N1 2.433(3), Bi1–N3 2.444(3); N1–Bi1–N3 83.99(11), N1–Bi1–Bi1A 72.35(8).

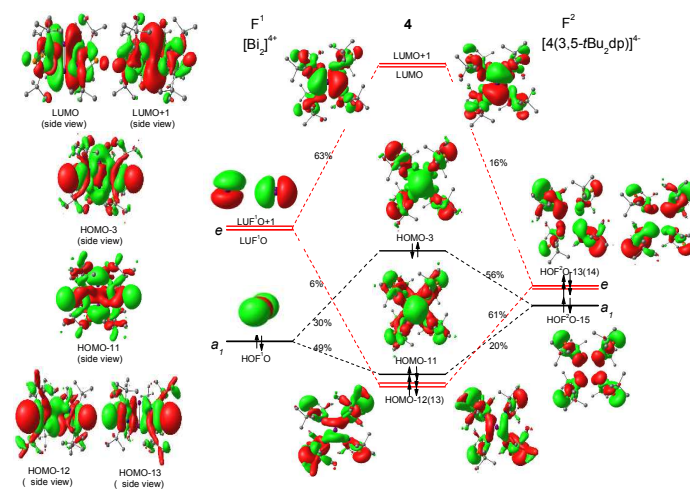
The reaction of  $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ <sup>24</sup> and **7** was carried out in toluene under reflux to elucidate the proposed one-electron oxidation process. After workup, the N–P coupling 1,2,4-diazaphospholyl dimer **10**,<sup>12b</sup> for which previous evidence had been obtained, was isolated as yellow crystals in ca. 17% yield.<sup>17</sup> We therefore concluded that the one-electron oxidation of  $\text{K}[3,5-R_2dp]$  by the Bi(III) ion proceeded via the neutral radical  $[3,5-R_2dp]^{\bullet}$ , favoring dimerization in toluene but hydrogen abstraction in THF.

To determine if complex **4** presents in a radical form such as  $[\text{L}^{\bullet}(\text{Bi}=\text{Bi})\text{LL}^{\bullet}]$  ( $\text{L} = \{\eta^1, \eta^1-3,5-t\text{Bu}_2dp\}$ ,  $\text{L}^{\bullet} = \{\eta^1, \eta^1-3,5-t\text{Bu}_2dp\}^{\bullet}$ ), in which the Bi=Bi bond distance should be close to 2.82  $\text{\AA}$ . However, the EPR spectra of **4** are silent even at low temperatures (77K), negating such a possibility. The APT<sup>25</sup> charge calculated value for each Bi atom is 2.03, suggesting the +2 valence of Bi atom in **4**. The Bi–Bi single bond feature in **4** is also confirmed by the calculated Mayer bond index (0.724409) and Wiberg bond index (0.8562).<sup>26</sup>

We next aimed to improve our understanding of the characteristic of the bonds between the  $[\text{Bi}=\text{Bi}]^{4+}$  unit and the coordinating  $[3,5-R_2dp]^{-}$  ligands ( $R = tBu, iPr, \text{ or } Ph$ ) and to determine the principal origin of the remarkably shortness of the Bi–Bi bonds in **4**, **5**, and **6**. We optimized the geometry (close to  $D_4$  symmetry) of **4** using the B3LYP method,<sup>27,28</sup> using the 6-31G(d) basis set for C, H, N and P atoms and LanL2dz basis set and pseudo potential for the Bi atoms. We analyzed the orbital components of the six molecular orbitals (two  $a_1$  orbitals and four  $e$  orbitals) that made the dominant contributions to the bonds between the  $(\text{Bi}_2)^{4+}$  unit (denoted by  $F^1$ ) and the four coordinating 1,2,4-diazaphospholides  $\{4[3,5-t\text{Bu}_2dp]\}^{4-}$  (denoted by  $F^2$ ). To achieve this, we used the charge deposition analysis (CDA) method<sup>29</sup> in the Multiwfn 3.3.8 software packages.<sup>30</sup> The fragment orbital interaction diagrams for these key molecular orbitals are shown in Figure 4.

As shown in Figure 4, HOMO-11 and HOMO-3 were found mainly to form through bonding and antibonding interactions between the  $a_1$ -bond of Bi–Bi fragment and the  $a_1$  orbital of the four  $[3,5-t\text{Bu}_2dp]^{-}$  ligands. The fragment orbital of the coordinating  $[3,5-t\text{Bu}_2dp]^{-}$  ligands ( $\text{HOF}^2\text{O}-15$ , 20%) in HOMO-11 were found to have positive bonding interaction with the middle region of Bi–Bi-bonding orbital ( $\text{HOF}^1\text{O}$ , 49%). The in-plane fragment orbital of the

coordinating  $[3,5-t\text{Bu}_2dp]^{-}$  ligands ( $\text{HOF}^2\text{O}-15$ , 56%) in HOMO-3 were found to have positive bonding interaction with the top and bottom regions of the Bi–Bi-bonding orbital ( $\text{HOF}^1\text{O}$ , 30%). The relative short distances of the N–N bond in the four  $[3,5-t\text{Bu}_2dp]^{-}$  ligands were found to cause the HOMO-11 and HOMO-3 bonding interactions between  $(\text{Bi}_2)^{4+}$  and  $\{4[3,5-t\text{Bu}_2dp]\}^{4-}$  fragments to make an effect that pulls the two Bi atoms closer, leading the Bi–Bi distances to be very short.



**Figure 4.** MO-FO interaction diagram for the main interaction between  $[\text{Bi}=\text{Bi}]^{4+}$  unit ( $F^1$ ) and the four coordinating 1,2,4-diazaphospholides  $\{4[3,5-t\text{Bu}_2dp]\}^{4-}$  ( $F^2$ ). The orbital energy levels of  $F^1$  were shifted with a vshift of 24 eV, while the orbital energy levels of  $F^2$  were shifted with a vshift of  $-11$  eV.

In addition to the  $a_1$  type HOMO-3 and HOMO-11, two  $e$  type molecular orbitals, HOMO-12 and HOMO-13, made minor contributions to the shortness to the Bi–Bi bond. HOMO-12 and HOMO-13 are found to be formed through the bonding interactions between the two unoccupied  $e$  orbitals of  $[\text{Bi}=\text{Bi}]^{4+}$  ( $\pi$ -bonding orbitals,  $\text{LUF}^1\text{O}$  and  $\text{LUF}^1\text{O}+1$  1.6%) with the two occupied  $e$  orbitals of  $\{4[3,5-t\text{Bu}_2dp]\}^{4-}$  ( $\text{HOF}^2\text{O}-13$  and  $\text{HOF}^2\text{O}-14$ , 61.0%). We found that antibonding interaction between  $\text{LUF}^1\text{O}/\text{LUF}^1\text{O}+1$  and  $\text{HOF}^2\text{O}-13/\text{HOF}^2\text{O}-14$  results in there being an unoccupied  $e$  molecular orbital LUMO/LUMO-1.

Short Bi–Bi bond lengths were also found in **5** (2.862  $\text{\AA}$ ) and **6** (2.868  $\text{\AA}$ ). The Bi–Bi bond length increased in the order **4** 2.7964(4)  $\text{\AA}$  < **5** (2.862  $\text{\AA}$ )  $\approx$  **6** (2.868  $\text{\AA}$ ), and this order can be attributed to the steric effect of the substituent decreasing in the order  $t\text{Bu} > i\text{Pr} \approx Ph$ . This conclusion was supported by the experimental determined and the theoretical calculated Bi–Bi–N–N torsion angles in **4**, **5**, and **6**, which were 22.8°–27.0°/21.4°, 0.08°–4.1°/4.5° and 2.9°–4.8°/0.5°, respectively. The tilted five-membered ring plane in **4** was found to result in the projected N–N distance being shorter at the Bi–Bi bond, meaning that the ligands will pull the two bismuth atoms closer together. The calculated bond lengths and angles match the values found in the experimental (ESI).<sup>17</sup>

In conclusion, we developed a simple redox pathway for preparing a family of rare paddlewheel 1,2,4-diazaphospholide dibismuthanes (**4–6**) with very short Bi–Bi bonds. The Bi–Bi bond in **4** is even shorter than the Bi=Bi double bonds in dibismuthenes.<sup>5</sup> The ability to successfully prepare **4–6** was apparently caused by the unique electronic nature of the ligands.<sup>10,11,12</sup> This suggested that the

extensive p,d-block paddlewheel 1,2,4-diazaphospholide complexes and the related paddlewheel heterodimetallic compounds are possible.<sup>9</sup> Work is proceeding along these lines.

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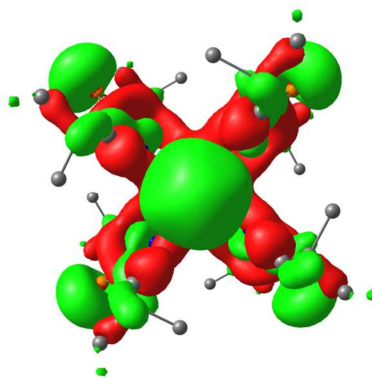
Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

The homoleptic 1,2,4-diazaphospholide paddlewheel bismuthanes (I, II $\alpha$ , II $\beta$ , III) have very short Bi–Bi bonds (left), which was caused by the interactions between Bi–Bi  $\sigma$  bonding orbital and  $a_1$  orbitals of the ligands and the short N–N bonds in the  $\eta^1, \eta^1$ -bridged ligands (right, HOMO-11).

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**Paddlewheel 1,2,4-Diazaphospholide Dibismuthanes with Very Short Bismuth–Bismuthane Single Bonds**