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# 1,2,4-Triazolato paddlewheel dibismuth complexes with very short Bi(II)-Bi(II) bonds: bismuth(III) oxidation of 1,2,4-triazolato anions into neutral N-1,2,4-triazolyl radicals

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Bismuth(III) oxidation of 3,5-di-substituted-1,2,4-triazolato anions afforded paddlewheel 1,2,4-triazolato dibismuth complex [L<sub>2</sub>(Bi–Bi)L<sub>2</sub>] (L =  $\eta^1, \eta^{1-3}, 5-R_2tz$ , R = Ph (3), *i*Pr (4)) with very short Bi(II)-Bi(II) bonds (2.8650(4)–2.8721(3) Å). The reaction involved the intermediates of organobismuth radical [Bi(R<sub>2</sub>tz)<sub>2</sub>]<sup>•</sup> and neutral *N*-1,2,4-triazolyl radical [3,5-R<sub>2</sub>tz]<sup>•</sup>. The dimerization of the former produced the corresponding dibismuth complex while the latter was trapped by spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) to give the radical adduct of {(3,5-R<sub>2</sub>tz)(DMPO)}<sup>•</sup> which was unambiguously evidenced by EPR analysis.

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 dibismuth complexes 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. 3.0884(4) Å (the covalent radii are 3.5453(4) Å).3 paddlewheel The first p-block complex. dibismuth(trifluoroacetate)<sub>4</sub> with a Bi-Bi single bond of 2.95 Å,<sup>4</sup> showed the unique electronic structure and bonding characteristic in comparison to those in *d*-block paddlewheel complexes.<sup>5</sup> Such paddlewheel dibismuth complex has been used as a precursor for several novel heterobimetallic complexes, 6a-g and some of which have proved to be efficient catalysts in organic transformations.<sup>6h-j</sup> Recently, we developed a very straightforward strategy for the preparation of paddlewheel dibisthmuth complexes<sup>7,8</sup> and distibines9 with aromatic five-membered heterocyclic 1,2-diaza-4phospholide<sup>7,9</sup> and pyrazolato<sup>8</sup> ligands.<sup>8-9</sup> In these reactions, bismuth(III)/antimony(III) ion was formally reduced by the fivemembered heterocyclic anions instead of using additional reduced agents such as Zn, Mg, or even K. The mechanism for the formation of these unusual dibismuth complexes most likely involved organometallic radical intermediates. The dimerization of organometallic radical intermediates may allow the corresponding low-valent bismuth paddlewheel complexes to be isolated.<sup>8</sup> We thus felt that bismuth (III) oxidation of deprotonated five-membered heterocycles into the related neutral radicals and organobismuth(II) radical intermediates may be general. With this in mind, we turned our interest toward paddlewheel 1,2,4-triazolato dibismuth complexes induced by bismuth(III) ion. In this contribution, we reported two paddlewheel 1,2,4-triazolato dibismuth complexes with very short Bi-Bi single bonds that are close to the reported Bi=Bi double bond lengths (ca. 2.82 Å) in dibismuthenes RBi=BiR.<sup>2c-e</sup> The EPR analysis unambiguously demonstrated that the Bi(III) ion oxidized 1,2,4-triazolato monoanionic ions into the corresponding *N*-heterocyclic aromatic free radicals.

In a ratio of 1:3, the reaction of BiCl<sub>3</sub> and 1,2,4-triazolato potassium K[3,5-R<sub>2</sub>tz] (R = Ph (1)<sup>10a</sup>, and *i*Pr (2)<sup>10b,c</sup>) in tetrahydrofuran provided, after worked up, two paddlewheel dibismuth complexes {( $\eta^1, \eta^{1-3}, 5-R_2tz$ )<sub>2</sub>(Bi–Bi)( $\eta^1, \eta^{1-3}, 5-R_2tz$ )<sub>2</sub>] (R = Ph (3-toluene) and *i*Pr (4)) as orange crystals in a fair yield (30.2% for 3-toluene and 56.5% for 4) (Scheme 1, Figures S1-S4).<sup>11</sup> Concentrating the mother liquor allowed an additional portion of the dibismuth complex and the small amount of the protonated ligand H[3,5-R<sub>2</sub>tz] (R = Ph(5),<sup>12</sup> *i*Pr(6)<sup>13</sup>)(*vide infra*) to be isolated.<sup>7</sup> Complexes 3-toluene and 4 decomposed at 250°C and 260°C, respectively, and the crystals were only slightly re-dissolved in THF.



Scheme 1 The preparation of complexes 3 and 4

The X-ray diffraction analysis confirmed the dibismuth assembly  $[\{\eta^1,\eta^1-3,5-R_2tz\}_2(Bi-Bi)\{\eta^1,\eta^1-3,5-R_2tz\}_2]$  (R = Ph (**3·toluene**), and  $\mathit{i}Pr(\textbf{4})$ ) (Figures 1–2, Tables S1-S3) that crystallized in the triclinic

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space group P-1.11,14 As shown in Figures, the inversion center at the midpoint of Bi-Bi bond in each dibismuth complex and a total absence of axial interactions of any kind between the dibismuth units indicated that the overall 1,2,4-triazolato ligand arrangement around the Bi<sub>2</sub> core was an almost perfect paddlewheel structure. 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 **3** and **4** varied slightly, by ca. 0.01 Å around the average values (2.442(3) Å for 3, 2.4460(5) Å for 4) that are close to those (Bi-N 2.447(8)-2.466(5) Å) found in paddlewheel 1,2-diaza-4-phospholide dibismuth complexes (Bi<sub>2</sub>dp<sub>4</sub>) and paddlewheel pyrazolato dibismuth complexes (Bi2pz4) (Tables 1).<sup>7,8</sup> The Bi–Bi distances (2.8721(3) Å in 3 and 2.8650(4) Å in 4) are much shorter than that found in paddlewheel complex  $[Bi_2(O_2CCF_3)_4]$ (2.947(1) Å).<sup>4a</sup> The planes of 1,2,4-triazolato ligands in the face-toface orientation were almost perpendicular to each other, with an average dihedral angle of close to 90° despite the average N-Bi-N angle being 84.62(11)° in 3, 84.73(18)° in 4.



Fig. 1 X-ray crystal structure of 3-toluene. Drawn with ellipsoids at 30% probability, toluene molecule and hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles (deg). Bi(1)–Bi(2) 2.8721(3), Bi(1)–N(4) 2.422(3); N(1)-Bi(1)-Bi(1) 71.47(7).



Fig. 2 X-ray crystal structure of 4. Drawn with ellipsoids at 30% probability and hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles (deg). Bi(1)–Bi(1A) 2.8650(4), Bi(1)–N(1) 2.472(5); N(4)-Bi(1)-N(1) 84.23(18).

Table 1. Comparison of the selected bond distances (avg.)(Å) and angles (avg.)(°) for paddlewheel complexes 3, 4,  $Bi_2dp_4$ ,  $Bi_2pz_4$ , and  $Bi_2(O_2CCF_3)_4$ ]

|        | 3         | Bi₂dp₄    | Bi2pz4    | 4         | $Bi_2(O_2CCF_3)_4$ |
|--------|-----------|-----------|-----------|-----------|--------------------|
| Bi–Bi  | 2.8721(3) | 2.8873(3) | 2.8705(6) | 2.8650(4) | 2.947(1)           |
| Bi–N   | 2.442(3)  | 2.447(8)  | 2.464(8)  | 2.4460(5) | -                  |
| N-Bi-N | 84.62(11) | 84.35(11) | 84.58(18) | 84.73(18) | -                  |

The isolation of dibismuth complexes **3** and **4** suggested that a redox reaction occurred. We supposed that a homoleptic complex  $[Bi(R_2tz)_3]$  (I) formed at first in the reaction of BiCl<sub>3</sub> and K[R<sub>2</sub>tz] (1:3). As the heteroatoms are known to be effective at delocalizing spin density and concomitant stabilizing radicals,<sup>15</sup> one charge probably transferred from one of the ligands to the bismuth(III) centre to

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produce open-shell radicals  $[Bi(R_2tz)_2]^{\bullet}$  ((II) $^{\bullet}$ ) and  $[3,5_{-R_2tz}]^{\bullet}_{Cle}$ ((III) $^{\bullet}_{Cle}$ ) (Scheme 2). The radical (II) $^{\bullet}$  dimerized DandLOthers and Compared Call 34III)<sup>e</sup> abstracted H-atom from THF to give the corresponding paddlewheel dibismuth complex (3 or 4) and the protonated form H[3,5-R\_2tz]of the ligand, respectively.<sup>7</sup>



Scheme 2. The proposed radical intermediates in the reactions for the preparation of complexes 3 and 4 as well as the formation of {(III)(DMPO)} adduct.

To verify our hypothesis, performing the reaction under a similar condition but using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin trap (Scheme 2) gave two strong EPR spectra (Figure 3 and Figure S14).<sup>10</sup> Note that the spectra for the DMPO adducts of the C-, O-containing radicals usually presented a coupling quadruplet<sup>16</sup> whereas those of the Ncontaining radicals displayed a hyperfine of the coupling multiplet with 12 observed lines which have been recently evidenced by us<sup>8,17</sup> and others.<sup>18</sup> As shown in Figure 3, the spectrum for the product of the  $Bi^{3+}$ -oxidized  $[R_2tz]$  (R = *i*Pr) system in the presence of DMPO displayed a hyperfine of wellresolved coupling multiplet with 12 observed lines which were assigned to the adduct of {(III<sup>,Pr</sup>)(DMPO)}. This clearly suggested that N-1,2,4-triazolato radical ( $III^{iPr}$ )• formed.<sup>11</sup> The distinction between a nitrogen coupling constant aN = 17.29 G, a proton splitting of aH = 13.19 G and a second nitrogen splitting aN'= 3.81G suggests a  $\sigma$ -type of *N*-triazolyl spin adduct structure on the basis of the linewidth of the signals (g = 2.007). The coupling constants aN, aH, and aN' of the {(III<sup>/Pr</sup>)(DMPO)} adduct were comparable to those of {(3,5-tBu<sub>2</sub>dp)(DMPO)}, {(3,5tBu<sub>2</sub>pz)(DMPO)}<sup>•</sup>, and {(N-tetrahydroyl-pz)(DMPO)}<sup>•</sup> species (Tables 2).<sup>17,7,18a</sup> However, the EPR spectrum of {(III<sup>Ph</sup>)(DMPO)}• is too complicated to get the corresponding accurate parameters (Figure S14), which may result from the overlapped signals by the two resonant electronic isomers of 3,5-dipheny-1,2,4-triazolyl radicals {(**III**<sup>Ph</sup>)(DMPO)}• (Chart 1, σ-type).



Fig. 3 X-band EPR spectrum of  $(3,5-iPr_2tz)DMPO^{\bullet}$  adduct  $(7^{iPr})$  in anhydrous THF with  $Bi^{3+}$ 

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**Table 2.** The comparison of the coupling constants (*a*) and *g* factors of {(3,5-*i*Pr<sub>2</sub>tz)(DMPO)}\*, {(3,5-*t*Bu<sub>2</sub>pz)(DMPO)}\*<sup>[8]</sup> and {(3,5-*t*Bu<sub>2</sub>dp)(DMPO)}\*<sup>[17]</sup> adducts in anhydrous THF

| Items                                       | a <sub>N</sub> | a <sub>H</sub> | a <sub>N'</sub> | g     |
|---|----------------|----------------|-----------------|-------|
| {(3,5- <i>i</i> Pr <sub>2</sub> tz)(DMPO)}• | 17.29          | 13.19          | 3.81            | 2.008 |
| {(3,5-tBu <sub>2</sub> pz)(DMPO)}•          | 13.48          | 13.19          | 4.10            | 2.012 |
| {(3,5- <i>t</i> Bu <sub>2</sub> dp)(DMPO)}• | 14.70          | 14.70          | 3.43            | 2.007 |
|   |                |                |                 |       |



To further elucidate the redox property of 1,2,4-triazolato ions  $[3,5-R_2tz]^-$ , the cyclic voltammetric analyses of **1** and **2** were performed in the presence of Bu<sub>4</sub>N·PF<sub>6</sub>. As shown in Figure S13, only one electron irreversible oxidation wave was observed for  $[3,5-Ph_2tz]^-/[3,5-Ph_2tz]^*$  at about  $E^{ox} = +1.20$  V vs AgNO<sub>3</sub>/Ag, probably suggesting that 1,2,3-triazolato anion  $[3,5-Ph_2tz]^-$  is oxidized at moderate positive potentials. However, no any significant oxidation/reduction waves were detectable for **2** (Figure S12).

Although triazolyl radicals have attracted attention for a long time, only few of the related reports appeared in literatures.<sup>19,20</sup> Lamotte and co-workers reported a 2,5dihydro-1H-1,2,4-triazol-2-yl neutral radical {H<sub>2</sub>[tz]•} which was created by gamma-irradiation of single crystals of 1,2,4triazole {H[tz]}.19a,b This radical was confirmed by analysis of the measured proton hyperfine tensors of ENDOR EPR spectra (Chart 2. B). After that, by using  $Ag_2O$ ,  $PbO_2$ , or  $K_3Fe(CN)_6$  as an oxidant, Neugebauer et. al. prepared several similar neutral radicals<sup>20a,b</sup> 2,3(2,5)-dihydro-1*H*-1,2,4-triazol-l-yl through dehydrogenation of 4,5-dihydro-1H-I,2,4-triazoles, and one of which was confirmed by X-ray single crystal structural analysis (Chart 2, B). Recently, a structurally characterized carboranefused 1,2,3-trizaolyl anion radical was synthesized by Co(II) reduction of a zwitterionic heterocyclic carborane-fused 1,2,3triazole (Chart 2, C).20c However, no any report for the primitive aromatic neutral radicals of the type 1,2,4-trizolyl (A) (Chart 1) appeared before this presentation, likely due to their high activity as to be difficult for the isolation.



The elemental analysis results agreed with the formula of dibismuth complex **4** (SI). However, we were not able to get the satisfied elemental analysis result of **3** because of partially toluene molecule loss in the lattice during the dry under the reduced pressure, as evidenced by the integration in the <sup>1</sup>H

NMR spectrum (Figure S1). The <sup>1</sup>H NMR (600 MHz, THE-decomposition of **3** and **4** showed rather broad speaks at 2the expected range of *i*Pr and Ph groups (SI). The absence of N–H signals at  $\delta = 10-11$  ppm and the correct integral in the <sup>1</sup>H NMR spectra, supporting the formation of **3** and **4** with a uniform coordination environment. The broad resonances were presumably attributable to the equilibrium between **3**(**4**) and the related radical species [Bi(R<sub>2</sub>tz)<sub>2</sub>]<sup>•</sup> (II)<sup>•</sup> in the solution or to the fair solubility in THF or even both.

To understand the bonding in the paddlewheel motif of 3 and 4, we optimized the complexes 3 and 4 by the B3LYP method with the 6-31G(d) basis set for C, H, and N atoms and Lanl2dz basis set and ECP for the Bi atoms (SI),<sup>21,22</sup> and SMD<sup>23</sup> solvation model (THF). The orbital interaction (Figure S11) between Bi24+ (fragment 1, F1) and  $[iPr_2tz]_4^{4-}$  (fragment 2, F2) was carried out by Charge Decomposition Analysis (CDA) method, on a  $D_4$  symmetric geometry of complex 4. CDA results showed that, in the formation of complex 3, filling the electrons from highest occupied fragmental orbitals of  $[iPr_2tz]_4^4$  (F2) into the lowest unoccupied F1 orbitals stabilizes the formation of complex 4. Detailed analysis revealed that about 14% LUF10/LUF10' (e presentation), 15.5% LUF1O+1/LUF1O+1' (e presentation) and 10 % LUF1O+2 (a2 presentation) of Bi24+ (F1) was filled by the electrons from occupied orbitals of [*i*Pr<sub>2</sub>tz]<sub>4</sub><sup>4-</sup> (F2). This means that the very short Bi-Bi bond distances arise from the electronic effect of the N-N bond within the 1,2,4-triazolato ligands, which pull the two Bi atoms closer. In other words, the shorter N-N bonds of the 1,2,4-triazolato ligands relative to the O-O bond distance in dibismuth(trifluoroacetate)<sub>4</sub> are responsible for the short Bi-Bi bond in 3 and 4, as they were supported by four bridged ligands with the smaller Bi-Bi-N angles (about 72°(SI)) in 3 and 4, in comparison to those in dibismuth(trifluoroacetate)<sub>4</sub> with larger Bi-Bi-O angles (ca. 81°).4

We also calculated the Gibbs free energy required for the homocleavage from the proposed intermediate  $[Bi(R_2tz)_3]$  ( $I^{Ph}$  or  $I^{iPr}$ ) to radical species  $[Bi(R_2tz)_2]^{\bullet}$  (( $II^{Ph})^{\bullet}$  or ( $II^{iPr})^{\bullet}$ ) and  $[3,5-R_2tz]^{\bullet}$  (( $III^{Ph})^{\bullet}$  or ( $III^{iPr})^{\bullet}$ )(Tables S6-S11). The calculated bond dissociation energy for the process is only 26.49 kcal/mol for  $I^{Ph}$ . Based on the results, the former transformation seemed to be accessible much easier. Obviously, this is due to the delocalized electronic effect of phenyl groups at the radical intermediate. The formation of  $[Bi(R_2tz)_2]^{\bullet}$  (( $II^{Ph})^{\bullet}$  or ( $II^{iPr})^{\bullet}$ ) from an assumed intermediate [CIBi( $R_2tz$ )<sub>2</sub>] (R = Ph/iPr) by the cleavage of Bi–Cl bond can be ruled out since the calculated bond dissociation energy is much higher (58.92 or 58.79 kcal/mol) (Tables S18 and S19).

Considering that the open-shell five-membered free radicals are prone to dimerize through heteroatoms at which the single electron is located,<sup>17</sup> it was possible that the resultant radicals (III<sup>Ph</sup>)• or (III<sup>iPr</sup>)• immediately dimerized into III<sup>Ph</sup>–III<sup>Ph</sup> or III<sup>iPr</sup>–III<sup>iPr</sup> dimer after the generation. We therefore calculated the relative stability of the expected dimer derived from (III<sup>Ph</sup>)• or (III<sup>iPr</sup>)• radical at the B3LYP/6-31G(d) level, and the results suggested that dimer III(N1)-III(N2) through N1–N2 coupling (Figures S5,S8) is more stable one, which was located 12.9/7.8 kcal/mol lower than dimer III(N1)-III(N4) through N1–N4 coupling, respectively (Figures S6, S9). The calculated Bi–Bi bond distances in **3** (2.8721 Å) and **4** (2.865 Å) are well in agreement with the experimental values (Tables S2–S5). However, the proposed dimeric III(N1)-III(N2) through N1–N2 coupling awaits further experimental demonstration.

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### Conclusions

In conclusion, we prepared two paddlewheel bismuth complexes (**3**–**4**) with the very short Bi–Bi single bonds, which are the first examples of bismuth(II) paddlewheel complexes bearing 1,2,4-triazolato ligands. The neutral 3,5-substituted *N*-1,2,4-triazolyl radical [3,5-R<sub>2</sub>tz]• (III)• was unambiguously confirmed by EPR spectrum analysis. The nitrogen coupling constants of the EPR spectrum suggested that the unpaired electron of 1,2,4-triazolyl radicals is localized at the nitrogen atoms with a  $\sigma$ -type ground state ( $\sigma$ ) instead of over the fivemembered ring with a  $\pi$ -type ground state ( $\pi$ ).<sup>24</sup> Our work demonstrated that the neutral aromatic *N*-1,2,4-triazolyl radicals (**A**) were accessible by bismuth(III) oxidation of two symmetric 1,2,4-triazolato anions, strongly suggesting that bismuth(III) oxidation of aromatic five-membered heterocyclic ring anions could be general.<sup>7-9</sup>

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## **Conflicts of interest**

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There are no conflicts to declare.

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Bismuth(III) oxidation of 3,5-di-substituted-1,2,4-triazolato anions allowed paddlewheel 1,2,4-triazolato dibismuth complexes  $[L_2(Bi-Bi)L_2]$  (L =  $\eta^1, \eta^{1-3}, 5-R_2tz$ , R = Ph (**3**), *i*Pr (**4**)) with very short bismuth-bismuth bonds (2.8650(4)–2.8721(3) Å) to be isolated and the reaction involved the formation of neutral *N*-1,2,4-triazolyl radicals [3,5-R\_2tz]<sup>•</sup> that were evidenced by EPR analysis.