Inorganic Chemistry

Direct Evidence for Neutral N-Pyrazolyl Radicals: Paddlewheel Dibismuthanes Bearing Pyrazolato Ligands with Very Short Bi-Bi **Single Bonds**

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Supporting Information

ABSTRACT: Neutral *N*-pyrazolyl radicals [3,5-R₂pz][•] as reactive intermediates were generated by one-electron oxidization of the corresponding 3,5-disubstituted pyrazolato anions $[3,5-R_2pz]^-$ (R = *t*Bu, Ph) with BiCl₃ and trapped by the use of 5,5-dimethyl-1-pyrroline-N-oxide as a spin trap, which was confirmed by electron paramagnetic resonance spectral analysis. With dimerization of the postulated pyrazolato low-valent Bi^{II} radical species, two novel paddlewheel pyrazolatodibismuthanes $[L_2(Bi-$ Bi)L₂ [L = η^1, η^1 -3,5-R₂pz; R = tBu (5 α , 5 β , and 5 γ), Ph (6)] were isolated and structurally characterized.

The aromatic neutral five-membered ring radicals have attracted great interest in fundamental chemistry,1organometallics,^{4,5} and physical chemistry.⁶ Deprotonated 3,4,5-substituted pyrazoles with the aromatic 6π electronic structure $[3,4,5-R_1R_2R_3pz]^-$ (1; R_1 , R_2 , $R_3 = H$, alkyl, aryl, etc.; Scheme 1) are the heterocyclic analogues of the cyclo-

Scheme 1. N-Pyrazolyl Radicals (2) with σ - or π -Type Structures



pentadienyl ligand $\left[Cp^{-}/(Cp^{*})^{-} \right]$ and have been extensively applied to metal complexes as spectator ligands for many years.⁷⁻¹² The electron distribution within the heterocycle, however, presents a charge shift toward the more electronegative N atom, so that σ coordination with N1 or N2 or both is common in pyrazolato complexes.⁷ Because heteroatoms are

known to be effective at delocalizing the spin density and concomitantly stabilizing radicals,¹³ pyrazolato ions thus have high potential to electronically stabilize the radical 2,^{14,15} which may derived from the one-electron oxidation of 1.16,17

Although species **2** with possible $\sigma(2\sigma)$ and $\pi(2\pi)$ types has been theoretically postulated many times,^{14,15} it has not been evidenced directly so far because of its high reactivity. Louw and co-workers reported that thermolysis of tert-butyl-1pyrazolepercarboxylate and its 3-methyl derivative in a benzene solution at 140 °C leads to N-phenylated pyrazoles without the formation of isomeric C-phenyl derivatives.¹⁸ On the basis of this experimental fact, N-pyrazolyl radicals were, hence, postulated as intermediates, where the unpaired electron is delocalized over the two N atoms with a σ -type ground state (2σ) .¹⁸ However, no further evidence such as electron paramegnetic resonance (EPR) spectra for this radical species was provided. To date, the pyrazolyl radical structure with a σ (2σ) or π (2π) type is still a question of debate.

We have been interested in pyrazolato $\ensuremath{\mathsf{complexes}}^{19-21}$ and particularly in exploring the pyrazolyl radicals (2) that derive from the one-electron oxidation of 1 with hypervalent metal ions. Herein we report that neutral 3,5-substituted N-pyrazolyl radicals $[3,5-R_2pz]^{\bullet}$ (III) were generated by one-electron oxidization of the corresponding 3,5-disubstituted pyrazolato anions $[3,5-R_2pz]^ [R = tBu (3^-)$, Ph (4⁻)] with BiCl₃ (see Scheme 2 and the Supporting Information, SI). The radical species [3,5-tBu₂pz] (III) was trapped as a reactive intermediate by using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin trap to give a N-pyrazolyl radical adduct (9), which was confirmed by EPR spectral analysis.

The reaction between BiCl₃ and pyrazolatopotassium K[3,5- R_2pz] [R = tBu (3),¹⁹ Ph (4)²²], at a ratio of 1:3, in tetrahydrofuran (THF) resulted in an orange solution at room temperature (Scheme 2).²³ The solution was worked up, and the paddlewheel dibismuthane $\{(\eta^1, \eta^1-3, 5-R_2pz)_2(Bi-Bi)(\eta^1, \eta^1-3, 5-R_2pz)_2(Bi-Bi)(\eta^2, \eta^2-3, 5-R_2pz)_2(Bi-Bi)(\eta^2-Bi)$ $3,5-R_2pz_2$ [R = *t*Bu (5), Ph (6)] was readily isolated as orange crystals in a fair yield (38.7% for 5 and 13.9% for 6).

Received: July 26, 2017

Scheme 2. Formation of 5–9 Involving N-Pyrazolyl (III) Radicals



Concentrating the mother liquor allowed an additional portion of the dibismuthane to be isolated and the related colorless free ligand $H[3,5-R_2pz]$ [R = *t*Bu (7),¹⁹ Ph (8)] to be isolated in low yield (11.1% for 7 and small amounts of 8).²² The air- and moisture-sensitive dibismuthanes 5 and 6 were soluble in common organic solvents and decomposed at 267 and 256 °C, respectively.

X-ray diffraction analysis confirmed the dibismuthane assembly $[\{\eta^1, \eta^1-3, 5-R_2pz\}_2(Bi-Bi)\{\eta^1, \eta^1-3, 5-R_2pz\}_2]$ [R = tBu (5), and Ph (6); Figures 1 and 2 and Tables S1–



Figure 1. X-ray crystal structures of 5α , 5β , and 5γ . Drawn with ellipsoids at 30% probability. *t*Bu groups and H atoms omitted for clarity. Selected bond distances [Å] and angles (deg). 5α : Bi(1)–Bi(2) 2.8189(6); N(1)–Bi(1)–Bi(2) 71.7(2). $s\beta$: Bi(3)–Bi(4) 2.8185(6); N(16)–Bi(4)–Bi(3) 71.5(2). 5γ : Bi(5)–Bi(6) 2.8183(6); N(24)–Bi(6)–Bi(5) 72.1(2).

S3].^{23,24} Complex 5 possessed three distinct but similar Bi₂ molecules $(5\alpha, 5\beta, \text{ and } 5\gamma)$. As can been seen from Figures 1 and 2, the inversion center was at the midpoint of the Bi-Bi bond in each dibismuthane 5α , 5β , 5γ , and 6. This indicated that the overall ligand arrangement around the Bi₂ core was an almost perfect paddlewheel structure for 6 but a twisted structure (because of steric substituent repulsion) for 5. A total absence of axial interactions of any kind between the dibismuth units in 5 and 6 was found. Each Bi 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 5α , 5β , 5γ , and 6 varied slightly, by ca. 0.03 Å around the average. The average Bi-N bond distance was ca. 2.455(9) Å for 5α , 2.460(8) Å for 5β , 2.458(9) for 5γ , and 2.464(8) Å for 6. These Bi-N bond lengths are close to those found for dibismuthanes [Bi-N 2.446(3)-2.484(6) Å].^{25,26} The Bi-Bi distances [2.8185(6) Å in 5 and 2.8705(6) Å in 6] were much shorter than that found in $[Bi_2(O_2CCF_3)_4] \cdot C_6Me_6$ $[2.947(1) \text{ Å}]^{25}$ and other dibismuthanes.²⁶ Notably, the Bi–Bi



Communication

Figure 2. X-ray crystal structures of 6. Drawn with ellipsoids at 30% probability. H atoms omitted for clarity. Selected bond distances [Å] and angles (deg): Bi(1)-Bi(1A) 2.8705(6), N(1)-Bi(1) 2.331(5); N(1)-Bi(1)-N(4) 87.55(18).

bond [2.8185(6) Å] in **5** was very short, even shorter than the Bi=Bi double bond distance of ca. 2.82 Å.²⁷ The planes of the pyrazolato 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 84.27(7)° in **5** α , **5** β , and **5** γ and 84.58(18)° in **6**, which are comparable to those found in the recently reported 1,2,4-diazaphospholide dibismuthanes [{ η^1 , η^1 -3,5-R₂dp}₂(Bi-Bi)-{ η^1 , η^1 -3,5-R₂dp}₂] [dp = 1,2,4-diazaphospholide; R = tBu (A), and Ph (B)]: 84.3(8)° for A and 84.35(11)° for B (Tables 1 and S12 and S13).¹⁶

The isolation of low-valent bismuth paddlewheel complexes 5 and 6 suggested that a redox reaction occurred. However, oxidation of $K^+[3^-]$ (or $K^+[4^-]$) by BiCl₃ produced an orange solution that gave no EPR signal (Scheme 2).

Performing the reaction under similar conditions but using DMPO as a spin trap gave a strong EPR signal corresponding to DMPO[3,5- tBu_2pz][•] adduct (9).²³ As shown in Figure 3, the spectrum for the Bi³⁺-oxidized system displays a hyperfine of well-resolved coupling multiplet with 12 observed lines. This clearly indicates that the radical species III formed.²³ The distinction between a nitrogen coupling constant $a_N = 13.48$ G, a proton splitting of $a_H = 13.19$ G, and a second nitrogen splitting $a_{N'} = 4.10$ G suggests a N-pyrazolyl spin adduct structure (σ -type) on the basis of the line width of the signals (g = 2.012).

The reaction of 3/4 with BiCl₃ is unusual. There were no examples that the pyrazolato anion could be oxidized into the corresponding neutral radical before this presentation. It seems that, probably by a self-redox reaction of pyrazolatobismuth (I), the resultant low-valent pyrazolatobismuth(II) radicals (II) dimerized to afford two corresponding novel paddlewheel pyrazolatodibismuthanes **5** and **6** (Scheme 2). Verify the oxidation ability of other hypervalent metal ions such as a Sb^{III} ion with pyrazolato ligands under similar conditions was not successful. Only a homoleptic complex $[Sb(\eta^2-3,5-tBu_2pz)_3]$ (10) with a slipped η^2 -coordination mode was isolated (Scheme S2 and Figure S1). Cyclic voltammetric analysis of **3** was performed in the presence of Bu₄N·PF₆, and a one-electron irreversible oxidation wave was found for $3^-/3^{\circ}$ at about $E^{\text{ox}} = +0.60$ V vs AgNO₃/Ag,²³ but the wave was not

Table 1. Comparison of the Selected Bond Distances and Angles for 5, 6, A, and B

	5	Α	6	В
Bi–Bi (Å)	2.8185(6)	2.7964(4)	2.8705(6)	2.8873(3)
Bi–N(avg.) (Å)	2.457(9)	2.481(8)	2.464(8)	2.447(8)
N-Bi-N(avg.) (deg)	84.27(7)	84.3(8)	84.58(18)	84.35(11)





Figure 3. X-band EPR spectrum of the adduct 9 in anhydrous THF with $\mathrm{Bi}^{3+}.$

significant (Figure S11), which may suggest that the pyrazolato anion could be oxidized.

The p-plock paddlewheel complexes with very short metalmetal bonds have attracted interest very recently.^{16,17} To understand the characteristic of the bonding and the paddlewheel motif in 5/6, we optimized complex 5 by the B3LYP method with the 6-31G(d) basis set for C, H, and N atoms and the Lanl2dz basis set for the Bi atom (see the SI),^{28,29} and the SMD³⁰ solvation model of THF. We also calculated the Gibbs free energy required for the homocleavage of [Bi(tBu_2pz)_3] (I) to afford the [Bi(tBu_2pz)_2]• (II) and III radicals. The calculated bond dissociation energy for this process is only 29.7 kcal/mol in THF, which seemed available at room temperature. The formation of II from the intermediate [ClBi(tBu_2pz)_2] by the cleavage of Bi–Cl bond can be ruled out because the calculated bond dissociation energy is 65.4 kcal/mol.

In addition, we calculated the relative stability of two expected dimers derived from the radical III dimerization at the B3LYP/6-31G(d) level, and the results suggested that the dimer III(N)–III(N) with N–N coupling (Figure S8) is the more stable one, which was located 5.1 kcal/mol lower than the dimer III(N)–III(C) with N–C coupling (Figure S9). The calculated Bi–Bi bond distance in 5, 2.814 Å, is in good agreement with the experimental value 2.818 Å (Table S12).

In conclusion, the paddlewheel bismuthanes 5 and 6 with the very short Bi–Bi single bonds are the first examples of bismuth(II) paddlewheel complexes bearing pyrazolato ligands. Most importantly, neutral 3,5-substituted pyrazolyl radicals III were confirmed by EPR spectral analysis, which demonstrated that the unpaired electron of the pyrazolyl radicals is delocalized at the two N atoms with a σ -type ground state (2σ) instead of over the five-membered ring with a π -type ground state (2π).¹⁸

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01902.

NMR spectra and computational details (PDF)

Accession Codes

CCDC 1559486–1559488 for **5**, **6** and **10** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

W.Z. gratefully acknowledges financial support from the National Natural Science Foundation of China (Grant 21272143) and Program for Changjiang Scholar and Innovative Research Team in University (Grant IRT1156). We also acknowledge the National Supercomputing Center in Shenzhen for providing computational resources and *Gaussian 09 D01*.

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