#### Small-Molecule Activation

### Nitric Oxide Insertion Reactivity with the Bismuth–Carbon Bond: Formation of the Oximate Anion, $[ON=(C_6H_2tBu_2O)]^{1-}$ , from the Oxyaryl Dianion, $(C_6H_2tBu_2O)^{2-}$

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**Abstract:** The first example of NO insertion into a Bi–C bond has been found in the direct reaction of NO with a Bi<sup>3+</sup> complex of the unusual  $(C_6H_2tBu_2-3,5-O-4)^{2-}$  oxyaryl dianionic ligand, namely, Ar'Bi $(C_6H_2tBu_2-3,5-O-4)$  [Ar' = 2,6- $(Me_2NCH_2)_2C_6H_3$ ] (1). The oximate complexes [Ar'Bi $(ONC_6H_2-3,5-tBu_2-4-O)]_2(\mu-O)$  (3) and Ar'Bi $(ONC_6H_2-3,5-tBu_2-4-O)_2$  (4)

were formed as a mixture, but can be isolated in pure form by reaction of NO with a Bi<sup>3+</sup> complex of the  $[O_2C(C_6H_2tBu_2-3-5-O-4]^{2-}$  oxyarylcarboxy dianion, namely, Ar'Bi- $[O_2C(C_6H_2tBu_2-3-5-O-4)-\kappa^2O,O']$ . Reaction of **1** with Ph<sub>3</sub>CSNO gave an oximate product with  $(Ph_3CS)^{1-}$  as an ancillary ligand,  $(Ph_3CS)(Ar')Bi(ONC_6H_2-3,5-tBu_2-4-O)$  (**5**).

#### Introduction

Nitric oxide, NO, is a simple heterodiatomic molecule that is critical in many areas of science and technology.<sup>[1]</sup> It is a significant component in the atmospheric chemistry of smog,<sup>[2]</sup> the industrial chemistry of nitric acid and its derivatives,<sup>[3]</sup> and the biological chemistry of physiological processes related to nerve im-

pulse, blood pressure, and immune systems.<sup>[4]</sup> The radical nature of NO allows both oxidation to  $(NO)^{1+}$  and reduction to  $(NO)^{1-}$  to occur, whereas in biological systems, a protonated form designated HNO is accessible.<sup>[5]</sup> Recently, the first example of an  $(NO)^{2-}$  complex was identified.<sup>[6]</sup>

Due to this extensive chemistry, the reactivity of NO has been thoroughly examined with most of the elements in the periodic table.<sup>[7]</sup> An exception is with bismuth, a metal that historically has been understudied.<sup>[8]</sup> We now report bismuth NO chemistry and specifically, the NO reactivity of the previously reported Ar'Bi(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-3,5-O-4), **1**,  $[Ar' = 2,6-(Me_2NCH_2)_2C_6H_3]$ , a Bi<sup>3+</sup> complex of the unusual oxyaryl dianion,  $(C_6H_2tBu_2O)^{2-.[9]}$ The reactivity of NO was of interest to probe the chemistry of the Bi–C bond of this dianionic ligand that is generated by C– H bond activation and rearrangement from the reaction of KOC<sub>6</sub>H<sub>3</sub>tBu<sub>2</sub>-2,6 with the NCN pincer stabilized bismuth dichloride, Ar'BiCl<sub>2</sub> (Scheme 1).<sup>[9]</sup> Complex **1** reacts with NO in contrast



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Scheme 1. Synthesis of  $Ar'Bi(C_6H_2tBu_2-3,5-O-4)$  (1) and the reaction between 1 and  $CO_2^{.[9,10]}$ 

to  $\mathsf{BiPh}_3$  which, when exposed to 1 atm of NO gas for 24 h, shows no reaction.

To fully identify the reaction products of this direct reaction of NO gas with the oxyaryl bismuth–carbon linkage in **1**, independent syntheses were carried out with the NO delivery reagent Ph<sub>3</sub>CSNO and with the previously reported bismuth complex of the oxyarylcarboxy dianion,  $[O_2C(C_6H_2tBu_2-3-5-O-4)]^{2-}$ , **2**, formed from **1** and CO<sub>2</sub> (Scheme 1).<sup>[10]</sup> This has led to the first examples of NO insertion into a bismuth–carbon bond, unusual NO insertion chemistry, and structural data on the quinoidal oximate ligand,  $[ON=(C_6H_2tBu_2O)]^{1-}$ .<sup>[11]</sup>

#### **Results and Discussion**

A red acetonitrile solution of the oxyaryl complex, Ar'Bi(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-3,5-O-4), **1**,<sup>[9]</sup> reacted with NO at 1 atm to form a dark green solution that contains multiple products identified by <sup>1</sup>H NMR spectroscopy. Reactions conducted at low temperature (-35°C) and with stoichiometric amounts of NO gas also gave complicated product mixtures. However, from the room temperature reaction, yellow crystals of [Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O)]<sub>2</sub>(µ-O) (**3**) were obtained at -30°C from the crude acetonitrile reaction mixture (Figure 1). Subsequently, yellow crystals of Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O)<sub>2</sub>, **4**, were obtained at





**Figure 1.** ORTEP<sup>[12]</sup> representation of  $[Ar'Bi(ONC_6H_2-3,5-tBu_2-4-O)]_2(\mu-O)$  (**3**) from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The two bismuth centers are bound by a bridging oxygen (O1).



**Figure 2.** ORTEP representation of Ar'Bi $(ONC_6H_2-3,5-tBu_2-4-O)_2$  (4) with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

room temperature from the same mother liquor (Figure 2). The structures of these products were defined by X-ray crystallog-raphy, and the NO insertion reaction chemistry is shown in Equation (1).



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[NO][X] reagents, such as [NO][BF<sub>4</sub>], are far more common than insertion reactions with nitric oxide gas.<sup>[14]</sup>

In Equation (1), the formal insertion of NO into the Bi–C bond of the  $(C_6H_2tBu_2-3,5-O-4)^{2-}$ dianion generates the oximate ligand,  $[ON=(C_6H_2tBu_2O)]^{1-}$ , which is present in both **3** and **4**. The sodium salt of this oximate has been described as an intermediate formed in solution in reactions of NO with phenolates,<sup>[11]</sup> but to our knowledge, it has not been previously isolated. Compound **3** contains two

[Ar'Bi(oximate)]<sup>1+</sup> moieties linked by a bridging oxide, whereas **4** contains two oximate units bound to a single  $[Ar'Bi]^{2+}$  moiety. Because the N–O bond order in the oximate is one, the oxyaryl dianion is formally oxidized and the NO reduced in the reaction. Conversion of the oxyaryl dianion in **1** to the oximate monoanion creates a charge imbalance at the Bi<sup>3+</sup> center allowing coordination of the oxide ligand in **3**. The origin of the oxide is unknown, but it could arise from another equivalent of NO acting as an oxygen-delivery agent. The presence of the two oxyaryl-dianion-derived oximate ligands in **4** indicates that ligand redistribution is occurring under the reaction conditions.

Because **3** and **4** were formed as a mixture shown in Equation (1), efforts were made to synthesize them in pure form from other precursors. The oxyarylcarboxy complex, Ar'Bi- $[O_2C(C_6H_2tBu_2-3-5-O-4)-\kappa^2O,O']$ , **2**, formed from **1** and  $CO_2$ ,<sup>[10]</sup> had previously been shown to undergo facile decarboxylation under mild conditions in a reaction with  $I_2$ ,<sup>[15]</sup> and therefore had the potential to act as a surrogate for **1**. Accordingly, its

reactivity with NO was examined. Compound **2** reacts with NO at atmospheric pressure to form an emerald green solution similar to that of the reaction mixture shown in Equation (1). Yellow crystals identified as **3** by X-ray crystallography were isolated in >90% yield [Eq. (2)], and allowed this oximate complex to be spectroscopically characterized in pure form (see below).

When the reaction was performed in deuterated solvents in

The reaction involves a relatively rare example of insertion into an M–X bond by NO gas.<sup>[7a]</sup> Although NO is highly reactive, it typically reacts<sup>[13]</sup> either as a) an oxidant to form complexes of  $(NO)^{1-}$ ; b) as a reductant to form complexes of  $(NO)^{1+}$ ; or c) as an oxide delivery agent. Migratory insertion of bound  $(NO)^{1\pm}$  ligands and insertion of  $(NO)^+$  by reaction with

a sealed J. Young NMR tube, free carbon dioxide could be observed in the <sup>13</sup>C NMR spectrum, confirming decarboxylation of the  $[O_2C(C_6H_2tBu_2-3-5-O-4)]^{2-}$  ligand in **2** as part of the reaction process.

The isolation of pure **3** allowed the development of a route to isolate **4**. Reaction of **3** with two equivalents of either

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[Et<sub>3</sub>NH][Cl] or Me<sub>3</sub>SiCl forms primarily one equivalent of Ar'BiCl<sub>2</sub> and one equivalent of **4**, as was identified by NMR spectroscopy and X-ray crystallography [Eq. (3)].



(2)

Again, ligand redistribution is apparently involved. Although a mixture was formed, as shown in Equation (3), separation is now possible, because Ar'BiCl<sub>2</sub> is much less soluble in THF, and this allows **4** to be isolated in 45% yield with respect to bismuth. It is fortunate that the kinetics of these reactions allow the isolation of **4**, because it also reacts with both [Et<sub>3</sub>NH][Cl] and Me<sub>3</sub>SiCl to make Ar'BiCl<sub>2</sub>.

An additional by-product isolated from Equation (2) was a small amount of the polymeric carbonate species [Ar'Bi( $\mu$ - $\kappa^1:\kappa^2-CO_3$ )]<sub>n</sub>, as was identified by X-ray crystallography.<sup>[16]</sup> Formation of the carbonate as a minor product is reasonable, because free CO<sub>2</sub> is observed in the reaction vessel, and oxide formation was observed in the NO reaction [Eq. (1)]. Resonances consistent with small amounts of (Me<sub>3</sub>Si)<sub>2</sub>O<sup>[17]</sup> and the silylated oximate, Me<sub>3</sub>SiON=(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O), were observed by <sup>1</sup>H NMR and GC-MS techniques when **3** was reacted with Me<sub>3</sub>SiCl.

Another approach to avoid the complicated mixture of products from the NO reaction [Eq. (1)] was to examine reactions with the alternative NO source,  $Ph_3CSNO$ .<sup>[18]</sup> This reagent reacted with 1 to form another fully characterized complex of the oximate ligand, the bright orange ( $Ph_3CS$ )(Ar')Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O) (5). This complex can be obtained cleanly in >90% yield [Eq. (4)] and was crystallographically identified (Figure 3). In this case, the "[Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O)]<sup>1+</sup>" unit was trapped by a ( $Ph_3CS$ )<sup>-</sup> ligand before ligand redistribution or coordination to oxide occurred, as was found in Equation (1). This demonstrates the value of the  $Ph_3CSNO$  reagent as a substitute for NO.

The structures of **3–5** contain  $[Ar'Bi]^{2+}$  moieties with conventional Bi–C(Ar') bond lengths ranging from 2.184(3) to 2.235(4) Å.<sup>[10]</sup> The 2.493(3) to 2.576(3) Å Bi–N bond lengths of the pincer arms in **4** and **5** are also typical for  $[Ar'Bi]^{2+}$  compounds.<sup>[10,16,19]</sup> However, in **3**, there is asymmetry in its Bi–N

bonds, in which one arm of each pincer ligand has typical bond lengths (2.629(4) and 2.636(4) Å), whereas the other is much longer (2.845(4) and 2.910(4) Å). The latter long bond lengths are still within the sum of the van der Waals radii of 3.9 Å, but suggest less interaction as is sometimes observed with  $Ar'Bi^{2+}$ complexes.<sup>[10,20]</sup> This is part of the flexible nature of the Ar' ligand.

The first structural data on the  $[ON=(C_6H_2tBu_2O)]^{1-}$  oximate ligand, obtained in complexes **3–5**, revealed metrical parameters that are consistent with the quiniodal structures drawn in Equations [1–4]. These are shown in Figure 4 in com-

parison with the dianionic ligands in 1 and 2. Two values are shown for each distance in 3 and 4, because they have two oximate ligands per molecule. Two of the C–C bonds in each of the  $[ON=(C_6H_2tBu_2O)]^{1-}$  ligands in 3–5 are in the 1.347 to 1.358 Å range of a double bond and the C–O bond lengths,

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**Figure 3.** ORTEP representation of  $(Ph_3CS)(Ar')Bi(ONC_6H_2-3,5-tBu_2-4-O)$  (**5**) from two perspectives, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

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Figure 4. Bond distances in the oximate ligands of compounds 3, 4, and 5 compared to the dianionic oxyaryl and oxyarylcarboxy ligands in 1 and 2, respectively. Compounds containing two oximate ligands (3 and 4) list both distances for each bond.

1.232 to 1.239 Å, are also in the double-bond range.<sup>[21]</sup> In contrast, structures of the dianionic ligands in **1** and **2** are more delocalized.

The analogous C–C distances in **1** and **2** are longer, 1.372(3) to 1.384(3) Å, as are the C–O bond lengths, 1.265(4) to 1.278(2).<sup>[10]</sup> The 1.315(4) to 1.336(4) Å C–N bonds in **3–5** are slightly longer than those typically found in organic oximes, R<sub>2</sub>C=NOH (1.281 Å),<sup>[21]</sup> and the 1.317(4) to 1.349(3) Å N–O bonds of the inserted (NO)<sup>1–</sup> moiety are in the single-bond range.<sup>[21]</sup>

Although the structural parameters are consistent in 3-5 and the Bi-C(Ar') distances of each are conventional, the Bi-O-(oximate) bonds vary significantly in the three complexes as do the Bi-O-N angles: 2.277(3) Å [108.6(2)°] and 2.284(3) Å [103.1(2)°] for 3, 2.295(2) Å [105.55(16)°] and 2.364(2) Å [99.81(17)°] for **4**, and 2.455(2) Å [95.82(18)°] for **5**. More acute Bi-O-N angles were found with the longer distances in 4 and 5. In comparison to these Bi-O lengths, the 2.053(3) and 2.090(3) Å Bi-O(oxide) distances in 3 are much shorter. The pairs of Bi-O(oximate) distances in 4 and the two Bi-O(oxide) distances in 3 show a surprising disparity within the pair considering they are from chemically equivalent bonds. In comparison, the Ar'Bi( $OC_6H_3R_2$ -2,6)<sub>2</sub> series have Bi–O bonds that fall in a narrow range: 2.2972(17) and 2.3068(17) Å for R=Me, 2.2969(16) and 2.3000(16) Å for R = iPr, and 2.350(3) and 2.321(3) Å for Ar'Bi(OC<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-2,6-Me-4)<sub>2</sub>.<sup>[9]</sup> The larger Bi-O distance in  ${\bf 5}$  may arise due to the large size of the  $(Ph_3CS)^{1-}$ ligand. However,  $[Ar'Bi(\mu-\kappa^1:\kappa^2-CO_3)]_n^{[16]}$  also has long Bi–O bonds of 2.402(7), 2.411(8), and 2.412(7) Å. Overall, these structures demonstrate the flexibility of the (Ar'Bi)<sup>2+</sup> unit to stabilize a diverse set of aryloxide-derived ligands with both localized and delocalized structures and variable Bi-O bond distances.

<sup>1</sup>H NMR spectroscopy on the pure oximate products showed a 1:1 ratio of [ON=(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O)]<sup>1-</sup> to Ar' resonances for 3 that is qualitatively similar to the spectrum of 4, which has a 2:1 ratio of resonances. The <sup>1</sup>H NMR spectrum of 5 differs in that the resonances of the methylene protons of the Ar' ligand are split as is found for 1,<sup>[10]</sup> as well as some other Ar'Bi2+ compounds in the literature.<sup>[9,10,22]</sup> Compounds 2-4 did not show this splitting of the Ar' ligand resonances, even though the solid-state structure of 3 showed two different types of Bi–N distances.

The UV/Vis spectrum of **3** showed a solvent dependence not found for **1**, **2**, **4**, and **5**. In THF and MeCN, complex **3** is green due to an absorption at  $\lambda = 639$  nm ( $\varepsilon = 2\,900 \text{ m}^{-1} \text{ cm}^{-1}$ )

in THF and 634 nm ( $\varepsilon = 1600 \text{ m}^{-1} \text{ cm}^{-1}$ ) in MeCN, in addition to the maxima at approximately 375 nm ( $80000 \text{ m}^{-1} \text{ cm}^{-1}$ ). The second absorption is not observed when **3** is dissolved in toluene, diethyl ether, or dichloromethane and **3** is yellow. In contrast, the yellow orange complexes, **1**, **2**, **4**, and **5**, each show only single maxima at  $\lambda = 467 \text{ nm}$  ( $6900 \text{ m}^{-1} \text{ cm}^{-1}$ ), 379 nm ( $61700 \text{ m}^{-1} \text{ cm}^{-1}$ ), 397 nm ( $37400 \text{ m}^{-1} \text{ cm}^{-1}$ ), and 357 nm ( $15700 \text{ m}^{-1} \text{ cm}^{-1}$ ), respectively. The large molar absorptivity values are consistent with  $\pi - \pi^*$  transitions.<sup>[23]</sup>

#### Conclusion

The reaction of NO with the oxyaryl dianion complex,  $Ar'Bi(C_6H_2tBu_2-3,5-O-4)$  (1), has provided the first example of NO insertion into a Bi-C bond. This has led to the first fully characterized examples of the oximate ligand,  $[ON=(C_6H_2tBu_2O)]^{1-}$  in three different molecules, namely, [Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O)]<sub>2</sub>(µ-O) (**3**), Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O) $_2$  (4), and (Ph $_3CS)(Ar')Bi(ONC_6H_2\mbox{-}3,5\mbox{-}tBu_2\mbox{-}4\mbox{-}O)$  (5). Although the C-C and C-O distances in these quinoidal oximates are similar, their Bi-O distances show surprising variation. The utility of carboxyaryloxy Ar'Bi[O<sub>2</sub>C(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-3-5-O-4)- $\kappa^2$ O,O'] and Ph<sub>3</sub>CSNO as synthetic substitutes for 1 and NO, respectively, was also demonstrated.

#### **Experimental Section**

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All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water by using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents were sparged with ultra high-purity (UHP) argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were

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dried over NaK alloy, degassed by three freeze/pump/thaw cycles, and vacuum transferred before use. <sup>1</sup>H NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers (13C NMR spectra on the 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. IR samples were prepared as KBr pellets on a Varian 1000 FTIR system. Elemental analyses were conducted on a PerkinElmer 2400 Series II CHNS elemental analyzer and proved to be problematic with the oximate complexes compared to other Ar'Bi complexes. Incomplete combustion was often observed and multiple samples had to be analyzed. Nitric oxide (NO) gas was purchased from Aldrich (98.5%) and was passed through two U-shaped glass columns connected in series and cooled to  $-78 \degree C$  before use. [Et<sub>3</sub>NH][Cl] ( $\geq$  99%) (Sigma–Aldrich) was used as Ph<sub>3</sub>CSNO,<sup>[18]</sup>  $Ar'Bi(C_6H_2tBu_2-3,5-O-4)$  (1),<sup>[10]</sup> purchased. and Ar'Bi[O<sub>2</sub>C(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-3–5-O-4)- $\kappa^2$ O,O'] (**2**),<sup>[10]</sup> were prepared according to the literature.

#### Reaction of Ar'Bi(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-3,5-O-4) (1) with NO

A 100 mL Schlenk flask fitted with a high-vacuum Teflon stopcock was charged with a red solution of 1 (100 mg, 0.17 mmol) in acetonitrile (10 mL). The flask was placed on a high-vacuum line, degassed, and charged with 1 atm of NO. After stirring at RT for 1 h, a dark green mixture was formed. The flask was degassed with three freeze/pump/thaw cycles and transferred to an argon-filled glovebox. Yellow crystals of  $[Ar'Bi(ONC_6H_2-3,5-tBu_2-4-O)]_2(\mu-O)$  (3) suitable for X-ray diffraction analysis were isolated from a concentrated acetonitrile solution at -30 °C. Subsequently, yellow crystals of Ar'Bi(ONC\_6H\_2-3,5-tBu\_2-4-O)\_2 (4) suitable for X-ray diffraction analysis were isolated from a concentrated acetonitrile solution in an NMR tube that was left at RT for two days.

#### Synthesis of $[Ar'Bi(ONC_6H_2-3,5-tBu_2-4-O)]_2(\mu-O)$ (3)

A Schlenk flask (100 mL) fitted with a high-vacuum Teflon stopcock was charged with a yellow suspension of 2 (100 mg, 0.154 mmol) in THF (12 mL). The flask was placed on a high-vacuum line, degassed, and charged with 1 atm of NO. After stirring at RT for 1 h, a dark red solution formed. The reaction mixture was stirred overnight and then degassed. Upon degassing a rapid color change to emerald green was effected. The flask was transferred to an argonfilled glovebox and the solvent was removed under reduced pressure to give 3 as a green solid (90 mg, 91%). <sup>1</sup>H NMR (500 MHz,  $[D_3]$  acetonitrile):  $\delta = 7.69 [d, 4H, m-(Me_2NCH_2)_2C_6H_3]$ , 7.55 [t, 2H, p- $(Me_2NCH_2)_2C_6H_3]$ , 7.36 [s, 2H, ON =  $(C_6H_2tBu_2O)]$ , 7.20 [s, 2H, ON = (C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O)], 4.20 [s, 8H, (Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 2.57 [s, 24H, (*Me*<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 1.29 [s, 18H, ON=(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O)], 1.20 ppm [s, 18H, ON=(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O)]; <sup>13</sup>C NMR (125 MHz, [D<sub>3</sub>]acetonitrile):  $\delta$  = 187.9, 156.0, 134.1, 130.8, 129.2, 116.6 [(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and ON=  $(C_6H_2tBu_2O)], \ 68.7 \ [(Me_2NCH_2)_2C_6H_3], \ 46.2 \ [br \ s, \ (Me_2NCH_2)_2C_6H_3],$ 36.2  $[q-ON=(C_6H_2(CMe_3)_2O)]$ , 35.8  $[q-ON=(C_6H_2(CMe_3)_2O)]$ , 30.1 ppm  $[ON=(C_6H_2(CMe_3)_2O)];$  IR (KBr):  $\tilde{v} = 2954$  s, 2924 s, 2858 s, 1604 m, 1453 s, 1357 s, 1296 s, 1247 s, 1103 m, 1060 m, 1016 s, 927 s, 883w, 840 m cm<sup>-1</sup>; elemental analysis calcd (%) for  $C_{52}H_{78}Bi_2N_6O_5$ (1285.16): C 48.60, H 6.12, N 6.54; found: C 47.11, H 6.02, N 6.35. Yellow crystals suitable for X-ray diffraction analysis were grown from a concentrated acetonitrile solution at -30 °C.

# Synthesis of Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O)<sub>2</sub> (4) from 3 and [Et<sub>3</sub>NH][Cl]

Solid [Et<sub>3</sub>NH][Cl] (26.6 mg, 0.19 mmol) was added to a stirred emerald green solution of  ${\bf 3}$  (124 mg, 0.10 mmol) in THF (10 mL). After

stirring overnight, the reaction mixture was a dark yellow solution. The solvent was removed under vacuum leaving off-white solids that were stirred in a THF/n-hexane (2:3) solution. White solids were separated from the yellow supernatant by centrifugation and dried. The insoluble white solids were identified as the known  $\rm Ar'BiCl_2~by~^1H~NMR~spectroscopy.^{[19]}$  The soluble fraction upon drying gave an orange sticky solid, which was washed with nhexane to give 3 as an orange solid (77 mg, 45% yield with respect to bismuth). <sup>1</sup>H NMR (500 MHz,  $[D_3]$  acetonitrile):  $\delta = 7.79$  [d, 2H, m-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 7.58 [t, 1 H, p-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 7.42 [s, 2 H, ON= (C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O)], 7.11 [s, 2H, ON=(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O)], 4.29 [s, 4H,  $(Me_2NCH_2)_2C_6H_3]$ , 2.65 [s, 12H,  $(Me_2NCH_2)_2C_6H_3]$ , 1.28 [s, 18H, ON=  $(C_6H_2tBu_2O)]$ , 1.22 ppm [s, 18H, ON =  $(C_6H_2tBu_2O)]$ ; <sup>13</sup>C NMR (125 MHz, [D<sub>3</sub>]acetonitrile):  $\delta = 187.9$ , 138.9, 132.9, 130.4, 129.2, 117.0, and 112.5  $[(Me_2NCH_2)_2C_6H_3 \text{ and } ON=(C_6H_2tBu_2O)]$ , 68.9  $[(Me_2NCH_2)_2C_6H_3]$ , 47.0 [br s,  $(Me_2NCH_2)_2C_6H_3]$ , 36.1 [q-ON=  $(C_6H_2(CMe_3)_2O)]$ , 35.6  $[q-ON = (C_6H_2(CMe_3)_2O)]$ , 29.8 ppm [ON = $(C_6H_2(CMe_3)_2O)];$  IR (KBr):  $\tilde{v} = 2957 \text{ s}, 2918 \text{ m}, 2867 \text{ m}, 1608 \text{ s},$ 1455 s, 1388w, 1356 s, 1299 s, 1248 s, 1091 m, 1055 s, 1014 s, 924 s, 883 m, 840 m, 746w, 709 m cm<sup>-1</sup>; elemental analysis calcd (%) for  $C_{40}H_{59}BiN_4O_4$  (868.92): C 55.29, H 6.84, N 6.45; found: C 55.65, H 7.13, N 6.44. Crystals of 3 suitable for X-ray crystallography analysis were grown from a concentrated acetonitrile solution at RT.

## Synthesis of Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O)<sub>2</sub> (4) from 3 and Me<sub>3</sub>SiCl

Neat Me<sub>3</sub>SiCl (25  $\mu$ L, 0.20 mmol) was added by microsyringe to a stirred emerald green solution of **3** (120 mg, 0.10 mmol) in THF (12 mL), which gave a rapid color change to yellow. After stirring overnight, the yellow reaction mixture was dried under reduced pressure, and the crude product was stirred in *n*-hexane (10 mL) for 1 h. Separation by centrifugation gave off-white insoluble material, which was identified as Ar'BiCl<sub>2</sub> by NMR spectroscopy.<sup>[19]</sup> The *n*-hexane-soluble yellow solids were identified as **4** by X-ray crystallography and NMR spectroscopy.

#### Synthesis of (Ph<sub>3</sub>CS)(Ar')Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O) (5) from 1

A green solution of Ph<sub>3</sub>CSNO (50 mg, 0.17 mmol) in THF (6 mL) was added to a stirred dark red solution of 1 (100 mg, 0.17 mmol) in THF (4 mL). The solution turned light orange after 1 h. After stirring overnight, solvent was removed under vacuum to give a red sticky solid. This crude product was washed with *n*-hexane to give 5 as a bright orange powder (140 mg, 93%). <sup>1</sup>H NMR (500 MHz,  $[D_6]$ benzene):  $\delta = 7.82$  [d, 6H, m- $(C_6H_5)_3CS$ ], 7.72 [s, 1H, ON= (C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O)], 7.66 [s, 1H, ON=(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>O)], 7.28 [d, 2H, m- $(\mathsf{Me}_2\mathsf{NCH}_2)_2\mathsf{C}_6\mathsf{H}_3],\ 7.14\ [\mathsf{m},\ \mathsf{6H},\ o\text{-}(\mathsf{C}_6\mathsf{H}_5)_3\mathsf{CS}],\ 7.02\ [\mathsf{t},\ \mathsf{3H},\ p\text{-}(\mathsf{C}_6\mathsf{H}_5)_3\mathsf{CS}],$ 6.96 [t, 1H, p-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] 3.85 [d, 2H, (Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 3.78 [d, 2H, (Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 2.13 [br s, 12H, (Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 1.62 [s, 9H,  $ON=(C_6H_2tBu_2O)]$ , 1.43 [s, 9H,  $ON=(C_6H_2tBu_2O)]$ . <sup>13</sup>C NMR (125 MHz,  $[D_6]$ benzene):  $\delta = 205.5$ , 187.1, 155.9, 152.7, 147.8, 134.3, 131.5, 130.3, 129.1, and 115.7 [(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and ON=  $(C_6H_2tBu_2O)$ ] 144.9  $[(C_6H_5)_3CS],$ 126.6  $[(C_6H_5)_3CS],$ 69.0  $[(Me_2NCH_2)_2C_6H_3]$ , 46.2 [br s,  $(Me_2NCH_2)_2C_6H_3$ ], 36.0 [ON= $(C_6H_2(CMe_3)_2O)],$ 35.6  $[q-ON=(C_6H_2(CMe_3)_2O)],$ 30.3 [ON=  $(C_6H_2(CMe_3)_2O)]$ . IR (KBr):  $\tilde{v} = 2954 \text{ m}$ , 2864 m, 1588 s, 1485 s, 1447 s, 1356 s, 1293 s, 1245 s, 1116 s, 1074 m, 1017 m, 940 s, 885w, 841 m, 745 m, 703 s cm<sup>-1</sup>; the sample for elemental analysis was recrystallized from THF as a THF solvate: elemental analysis calcd for C45H54BiN3O2S·C4H8O (982.09): C 59.93, H 6.36, N 4.28; found: C 60.78, H 6.08, N 3.56. Crystals suitable for X-ray crystallography were grown from a saturated acetonitrile solution at RT.

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#### Synthesis of (Ph<sub>3</sub>CS)(Ar')Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O) (5) from 2

A green solution of Ph<sub>3</sub>CSNO (26 mg, 0.08 mmol) in THF (2 mL) was added to a stirred yellow suspension of 2 (55 mg, 0.08 mmol) in THF (8 mL). After stirring overnight, the red reaction mixture was dried under reduced pressure to give a red sticky solid. After washing with *n*-hexane, the bright orange powder (70 mg, 90%) was identified as 5 by NMR spectroscopy.

#### X-ray data collection, structure determination, and refinement

Crystallographic information for complexes 3-5 is summarized in Table 1. Further details can be found in the Supporting Information, which contains details of the crystallographic data collection

Table 1. X-ray data collection parameters for [Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O)]<sub>2</sub>(µ-O) (3) Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O)<sub>2</sub> (4) and (Ph<sub>3</sub>CS)(Ar')Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5tBu<sub>2</sub>-4-0) (5).

	3	4	5
empirical	$C_{52}H_{78}Bi_2N_6O_5$	$C_{40}H_{59}BiN_4O_4$ ·CH <sub>3</sub> CN	C <sub>45</sub> H <sub>54</sub> BiN <sub>3</sub> O <sub>2</sub> S•CH <sub>3</sub> CN
formula			
formula weight	1285.16	909.94	951.00
<i>T</i> [K]	143(2)	143(2)	88(2)
crystal system	monoclinic	triclinic	monoclinic
space group	P2 <sub>1</sub> /c	РĪ	P2 <sub>1</sub> /c
a [Å]	9.8964(10)	13.398(3)	22.1393(11)
b [Å]	34.851(3)	13.517(3)	9.2381(5)
c [Å]	16.6025(16)	14.142(3)	22.8113(12)
α [°]	90	93.614(3)	90
β [°]	92.3244(14)	117.448(2)	110.1112(6)
γ [°]	90	97.173(3)	90
V [ų]	5721.6(10)	2233.9(9)	4381.0(4)
Ζ	4	2	4
$ ho_{ m calcd}$ [mg m $^{-3}$ ]	1.492	1.353	1.442
$\mu$ [mm <sup>-1</sup> ]	6.189	3.988	4.113
$R1^{[a]}$ [ $l > 2.0\sigma(l)$ ]	0.0326	0.0273	0.0301
wR2 <sup>[a]</sup> (all data)	0.0832	0.0631	0.0710
[a] Definitions: $\Sigma[w(F_o^2)^2]]^{1/2}$ .	$R1 = \Sigma   F_{o}  -  F_{c}  /\Sigma  F_{o} ,$		$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/$

and refinement, along with selected bond lengths and angles. CCDC-1012494 (3), CCDC-1012495 (4), and CCDC-1012496 (5) con-

tain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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### **FULL PAPER**

The first example of NO insertion into a Bi–C bond has been found in the direct reaction of NO with a Bi<sup>3+</sup> complex of the unusual (C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-3,5-O-4)<sup>2–</sup> oxyaryl dianionic ligand, namely, Ar'Bi(C<sub>6</sub>H<sub>2</sub>tBu<sub>2</sub>-3,5-O-4) [Ar' = 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]. The oximate complexes [Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O)]<sub>2</sub>(µ-O) and Ar'Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O)<sub>2</sub> were formed (see scheme), as well as (Ph<sub>3</sub>CS)-(Ar')Bi(ONC<sub>6</sub>H<sub>2</sub>-3,5-tBu<sub>2</sub>-4-O), by reaction with Ph<sub>3</sub>CSNO.



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#### Small-Molecule Activation

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Nitric Oxide Insertion Reactivity with the Bismuth–Carbon Bond: Formation of the Oximate Anion,  $[ON=(C_6H_2tBu_2O)]^{1-}$ , from the Oxyaryl Dianion,  $(C_6H_2tBu_2O)^{2-}$