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Facile Bismuth−Oxygen Bond Cleavage, C−H Activation, and Formation of a Monodentate Carbon-Bound Oxyaryl Dianion, $(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)^{2-}$

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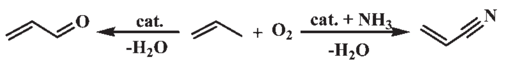
Supporting Information

ABSTRACT: The Bi^{3+} (*N,C,N*)-pincer complex $Ar'BiCl_2$ (**1**) [$Ar' = 2,6\text{-}(Me_2NCH_2)_2C_6H_3$], reacts with 2 equiv of $KOC_6H_3Me_2$-2,6 and $KOC_6H_3{}^iPr_2$-2,6 by ionic metathesis to form the anticipated bis(aryloxide) complexes $Ar'Bi(OC_6H_3Me_2\text{-}2,6)_2$ (**2**) and $Ar'Bi(OC_6H_3{}^iPr_2\text{-}2,6)_2$ (**3**), respectively. However, the analogous reaction with 2 equiv of $KOC_6H_3{}^tBu_2$-2,6 forms $HOC_6H_3{}^tBu_2$-2,6 and a dark-orange complex containing only one aryloxide-derived ligand bound via a Bi−C and not a Bi−O linkage. This complex is formulated as $Ar'Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)$ (**4**), a product of para C−H bond activation. Structural, spectroscopic, and DFT studies and a comparison with the protonated analogue $[Ar'Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}OH\text{-}4)][BPh_4]$ (**5**), which was obtained by treatment of **4** with $[HNEt_3][BPh_4]$, suggest that **4** contains an oxyaryl dianion. Complex **4** represents a fully characterizable product of a bismuth-mediated C−H activation and rearrangement of the type postulated in catalytic SOHIO processes.

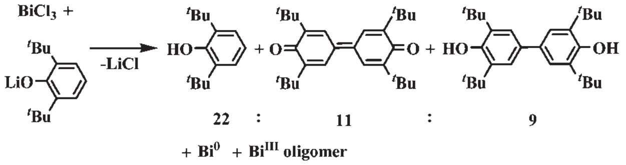
One fascinating use of bismuth[1−9] is as an essential component in the SOHIO process for the oxidation and ammoxidation of propene to form acrolein and acrylonitrile (Scheme 1) using multicomponent $Bi_2O_3 \cdot MoO_3$-based catalysts.[3]

Scheme 1. Propene Oxidation and Ammoxidation in the SOHIO Process



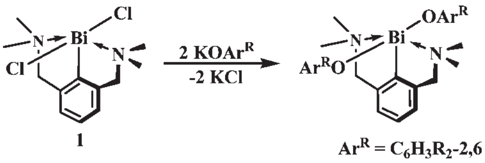
Current assessments of the mechanism of this catalysis[3,10] suggest that propene is initially bound to molybdenum in such a way that the allylic hydrogen can be transferred to an oxygen bound to bismuth, forming a π-allyl complex of molybdenum. Facile Bi−O bond homolysis subsequently leads to removal of the allyl hydrogen from the catalytic cycle. This scenario has been developed in extensive studies of both heterogeneous and homogeneous reactions, and a number of model systems have been reported. For example, Limberg and co-workers have reported complexes of allyloxy ligands such as $Bi(OCR_2CH{=}CH_2)_3$ (R = H or Me)[11] as well as examples of C−H activation in bimetallic Mo−Bi complexes.[12,13] Reactions of $BiCl_3$ with $LiOC_6H_3{}^tBu_2$-2,6 to form the products shown in Scheme 2 have been reported by Hanna and co-workers.[14,15] This is consistent with facile Bi−O bond homolysis and concomitant formation of an unstable Bi^{2+} radical.

Scheme 2. Products and Ratios of Bi−O Bond Homolysis Obtained by Hanna and Co-workers



As part of our investigations into the coordination chemistry of the $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi\}^{1+}$ cation for comparison with lanthanide cations,[16] we examined some Bi^{3+} complexes ligated by a single $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ ligand (Ar′).[17−21] Specifically, we sought to make $Ar'BiX_2$ complexes from the known $Ar'BiCl_2$ starting material[17] for comparison with the recently synthesized Ar'_2BiX species.[16] The X = $OC_6H_3{}^tBu_2$-2,6 case was of particular interest because this aryloxide anion acts as an outer-sphere ligand in $[Ar'_2Bi][OC_6H_3{}^tBu_2\text{-}2,6]$[16] and is the same aryloxide that displays the radical behavior reported by Hanna and co-workers.[15] Here we report on the unusual oxyaryl dianion product obtained by treatment of $Ar'BiCl_2$ with $KOC_6H_3{}^tBu_2$-2,6, its reaction chemistry to form a protonated analogue, and comparative reactions with aryloxides bearing alternative sets of substituents.

$Ar'BiCl_2$ (**1**) reacts with 2 equiv of $KOC_6H_3Me_2$-2,6 and $KOC_6H_3{}^iPr_2$-2,6 in THF to form $Ar'Bi(OC_6H_3Me_2\text{-}2,6)_2$ (**2**) and $Ar'Bi(OC_6H_3{}^iPr_2\text{-}2,6)_2$ (**3**), respectively (eq 1). Single crystal X-ray diffraction (XRD) studies of these yellow crystalline solids showed that both **2** and **3** (Figure 1) have conventional Ψ-octahedral[22] structures with the vacant site trans to the Bi−C bond of the tridentate (*N,C,N*) ligand as well as trans aryloxide ligation. The bond distances in **2** and **3** and the NMR spectral data are in the normal ranges, as detailed in the Supporting Information (SI).



(1)

$Ar^R = C_6H_3R_2$-2,6
R = Me, **2**; ^{i}Pr, **3**

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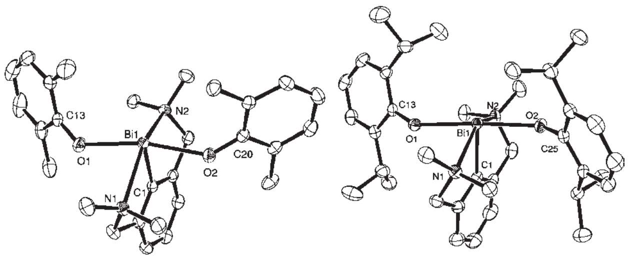


Figure 1. ORTEP[23] drawings of (left) $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(OC_6H_3Me_2\text{-}2,6)_2$ (**2**) and (right) $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(OC_6H_3{}^iPr_2\text{-}2,6)_2$ (**3**), with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. For **3**, only one of the two molecules in the asymmetric unit is shown.

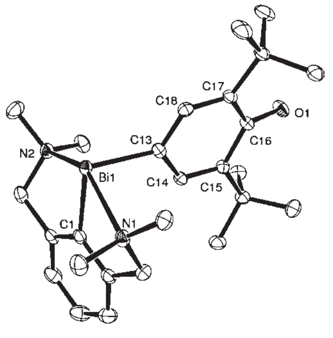
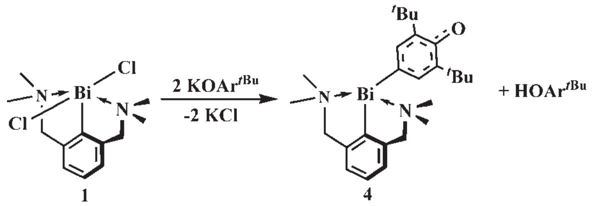


Figure 2. ORTEP drawing of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)$ (**4**), with ellipsoids drawn at the 50% probability level. Hydrogen atoms, the MeCN solvent molecule, and a second molecule of **4** present in the asymmetric unit have been omitted for clarity.

In contrast to the reactions in eq 1, the analogous reaction with $KOC_6H_3{}^tBu_2\text{-}2,6$ rapidly produced a dark-orange solution from which a dark-orange solid, **4**, was isolated (eq 2). This complex is formulated as $Ar'Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)$ on the basis of elemental analysis, spectroscopic characterization, and XRD.



(2)

The formation of $HOC_6H_3{}^tBu_2\text{-}2,6$ as a byproduct was suggested by the ^1H NMR spectrum of the crude material before crystallization. This was confirmed by ^1H NMR spectroscopy and GC−MS of the mother liquor following crystallization of **4**. The ^1H NMR spectrum of **4** contained the resonances expected for an asymmetrically coordinated Ar′ ligand[16−19] as well as a *tert*-butyl singlet of an intensity appropriate for just one ligand derived from the 2,6-di-*tert*-butylaryloxide reagent.

Recrystallization of **4** from MeCN gave X-ray-quality crystals that revealed the structure shown in Figure 2. Two independent molecules were found in the asymmetric unit (Figure S2 in the SI), and two sets of bond distances are discussed below. The bond distances were more consistent with the formulation of **4** as a Bi^{3+} complex of an oxyaryl dianion containing a conventional Bi−C(aryl) bond rather than a Bi^{2+} complex of an aryloxyl radical or a complex containing a Bi═C double bond. No evidence for hydrogen on the O1 atom was discernible from the X-ray data or by ^1H NMR or IR spectroscopy, and no EPR signal was observed for **4**.

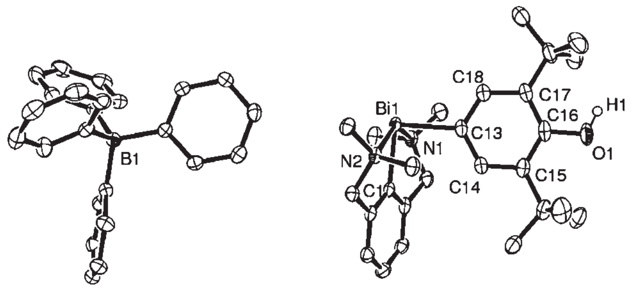
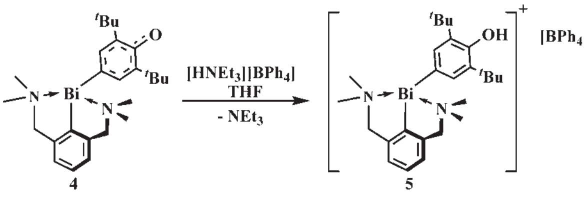


Figure 3. ORTEP drawing of $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}OH\text{-}4)\}[BPh_4]$ (**5**), with ellipsoids drawn at the 50% probability level. Hydrogen atoms (except H1) have been omitted for clarity.

To provide structural data for detailed comparison with the unusual dianionic $(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)^{2-}$ ligand in **4**, a monoanionic aryl phenol variant was prepared by treatment of **4** with 1 equiv of $[HNEt_3][BPh_4]$ in THF (eq 3). This rapidly formed a colorless solution that afforded the cationic complex $[Ar'Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}OH\text{-}4)][BPh_4]$ (**5**) (Figure 3 and Table S4 in the SI). As previously reported for $[Ar'_2Bi][BPh_4]$,[16] the $(BPh_4)^-$ anion in **5** does not interact with bismuth. As a result, **5** has the same coordination number and geometry around the bismuth center as in **4**, allowing a direct comparison of the metrical parameters.



(3)

The resonance for the OH proton in **5** was observable in the ^1H NMR spectrum, along with tetraphenylborate resonances and Ar′ resonances similar to those observed in **4**. The OH group had an observable sharp peak in the IR spectrum at 3608 cm^{-1}, which is within the typical spectral region expected for an OH stretch.

The 2.188(2) Å Bi1−C13 and 2.182(2) Å Bi2−C39 bond distances for the $(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)^{2-}$ ligand in **4** (Figure 4 and Table S3) are at the low end of the range for four-coordinate Bi−C(phenyl) single bonds in the literature [2.16(2)−2.30(2) Å],[24−27] but they are not significantly different from the typical tridentate (*N*,*C*,*N*) ligand Bi−C(Ar′) distances in **4** [Bi1−C1, 2.207(2) Å; Bi2−C27, 2.1987(19) Å].[16,17,28] In **5**, the analogous 2.221(3) Å Bi1−C13 length lies closer to the median value of the range for other Bi−C(phenyl) bond lengths. These distances suggest that the Bi1−C13 and Bi2−C39 lengths in **4** are closer to single bonds rather than double bonds.

The 1.278(2) Å C16−O1 and 1.275(2) Å C42−O2 bond lengths in **4** are significantly shorter than the 1.376(3) Å C16−O1 length in **5**, a distance that is typical for a C−O single bond in a phenol.[29−31] The C−O distances in **4** are closer to the double-bond distance of 1.246(10) Å in the quinone $p\text{-}O{=}(C_6H_2{}^tBu_2\text{-}2,6){=}O$[29] and the 1.246(2) Å C−O distance in the crystal structure of the radical $[OC_6H_2{}^tBu_3\text{-}2,4,6]$,[29] for which the most important resonance structure has quinoid character with C1═O, C2═C3, and C5═C6 double bonds and the unpaired electron at C4. The corrulene-based phenoxyl radical $[OC_6H_2{}^tBu_2\text{-}2,6\text{-}(C_{20}H_9)\text{-}4]$[32] and the triplet biradical

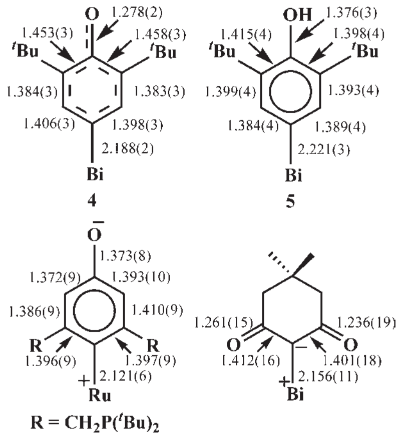


Figure 4. Comparison of selected bond lengths (Å) in **4**, **5**, $(CO)_2Ru[C_6H_2(CH_2P^tBu_2)_2\text{-}2,6\text{-}O\text{-}4]$, and $Ph_3Bi\{C[C(=O)CH_2]_2CMe_2\text{-}4\}$.

$[(OC_6H_2{}^tBu_2\text{-}2,6)_3C\text{-}4]$,[33] which also display a considerable degree of quinoid character, have similarly short C—O distances [1.250(2) and 1.24(1) Å, respectively].

The C—C bond lengths in the $(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)^{2-}$ ring in **4** are also similar to those in the above quinoid-like radicals $[OC_6H_2{}^tBu_3\text{-}2,4,6]$,[29] $[OC_6H_2{}^tBu_2\text{-}2,6\text{-}(C_{20}H_9)\text{-}4]$,[32] and $[(OC_6H_2{}^tBu_2\text{-}2,6)_3C\text{-}4]$.[33] For both molecules of **4**, the two ring bonds closest to oxygen have lengths of 1.453(3)—1.459(3) Å, the central ring bonds are 1.382(3)—1.384(3) Å, and the two C—C bonds closest to bismuth lie in the range 1.398(3)—1.407(3) Å. The analogous sequence of ring C—C bond lengths in the radical compounds listed above[26,29,30] is 1.468(2)—1.47(1), 1.36(1)—1.367(2), and 1.407(2)—1.42(1) Å, respectively. In contrast, all of the ring C—C lengths in **5** are more uniform [1.384(4)—1.415(4) Å; Figure 4] and are in the normal range for a phenol or phenoxide ligand.

The crystallographically characterized metal complexes in the literature that are closest to **4** are the metallaquinone $(CO)_2Ru[C_6H_2(CH_2P^tBu_2)_2\text{-}2,6\text{-}O\text{-}4]$[34] and the bismuth ylide $Ph_3Bi\{C[C(=O)CH_2]_2CMe_2\text{-}4\}$[35] (Figure 4). The ruthenium compound has a 1.373(8) Å C—O single bond in the solid state, consistent with a zwitterionic structure with the negative charge on oxygen and the positive charge on ruthenium. The solid-state structure of the latter bismuth compound also supports a zwitterionic model and has C—O distances of 1.23(2)—1.26(1) Å. Hence, the metalloquinoid-type structure of **4** is unusual.

The experimentally determined structures of **4** and **5** were evaluated by DFT calculations using the Tao—Perdew—Staroverov—Scuseria hybrid (TPSSh) functional.[36] Details of the computations are given in the SI. The optimized calculated bond distances for **4** and **5** are in good agreement with the crystallographic data (Tables S3 and S4). The calculated distances for the oxyaryl ligand in **4** show an alternating short—long pattern similar to that found experimentally (e.g., 1.456, 1.386, and 1.402 Å for C15—C16, C14—C15, and C13—C14, respectively). The short 1.280 Å C16—O1 distance also suggests significant double-bond character. In contrast, the calculated value for the protonated ligand in **5** shows a much longer C—O distance of 1.367 Å, which is consistent with a C—O single bond, and the C—C bond lengths calculated in the phenol ring in **5** are all very similar, as is typical for an aromatic phenyl ring. Frequency calculations on **4** predicted a strong absorption at 1539 cm^{-1} due to the coupled C—O and C—C stretches in the oxyaryl ligand (Figure S4). The intensity of this absorption was significantly diminished in the calculated IR spectrum of **5**. This is in agreement with the experimental data, in which a strong absorption at 1554 cm^{-1} was observed for **4** but was absent in the IR spectrum of **5**.

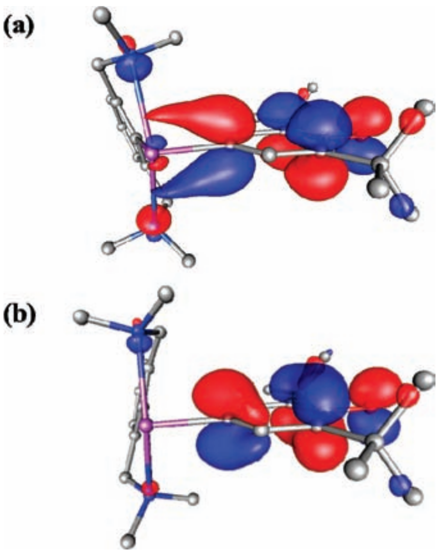


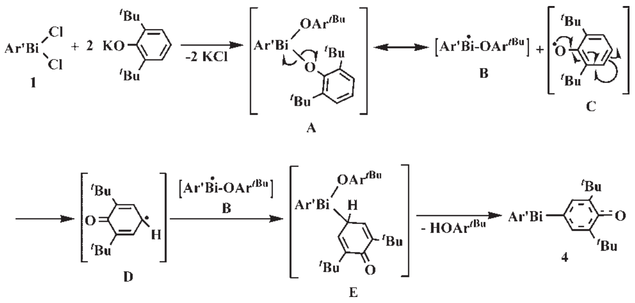
Figure 5. (a) HOMO of **4** showing electron density on the ipso carbon donating to bismuth. (b) HOMO of **5**. Both orbitals are drawn with a contour value of 0.04.

The highest occupied molecular orbital (HOMO) of **4** (Figure 5a) shows some donation of π-electron density from the ipso carbon atom of the oxyaryl ligand to bismuth, whereas the HOMO of **5** (Figure 5b) does not show such an interaction between these two atoms. Although this dative interaction is weak, it is consistent with a small contribution of a metalloquinone resonance form to the overall electronic structure of **4** and could account for the 0.02—0.05 Å experimental and 0.03 Å calculated difference between the Bi—C13 bond lengths in **4** and **5**. Natural population analysis (NPA) for **4** and **5** yielded an additional negative charge of 0.7 electrons for the oxyaryl ligand in **4** relative to the aryl phenol ligand in **5**, consistent with the formal dianionic assignment of the oxyaryl ligand in **4**. The lowest triplet electronic state was calculated to be 28 kcal/mol higher in energy than the closed-shell ground state, which is consistent with the lack of an EPR signal.

To examine the factors leading to the formation of **4**, several variations of eqs 1 and 2 were examined. To determine whether *tert*-butyl analogues of **2** and **3** could be obtained if the para C—H bond were not accessible for activation in the aryloxide, the reaction of 2 equiv of $KOC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4$ with $Ar'BiCl_2$ was examined. This formed an orange product from which the conventional bis(aryloxide) complex $Ar'Bi(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_2$ (**6**), analogous to **2** and **3** in eq 1, was isolated. XRD of **6** gave a structure that was consistent with the NMR and analytical data (Table S2 and Figure S3). Hence, it is possible to coordinate two 2,6-di-*tert*-butyl-substituted aryloxides to an $[Ar'Bi]^{2+}$ unit.

The importance of the steric bulk in the reaction system was demonstrated by the reaction of $Ar'BiCl_2$ with a mixture of 1 equiv of $KOC_6H_3{}^tBu_2\text{-}2,6$ and 1 equiv of $KOC_6H_3{}^iPr_2\text{-}2,6$. Only a trace amount of **4** was detectable by NMR in this reaction. A similar reaction involving $Ar'BiCl_2$ and a mixture of 1 equiv of $KOC_6H_3{}^tBu_2\text{-}2,6$ and 1 equiv of $KOC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4$ formed **4** as the main product by NMR analysis, indicating that formation

Scheme 3. Possible Mechanism for the Formation of 4 [Ar′ = 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]



of **4** requires two 2,6-di-*tert*-butyl-substituted aryloxides, but only one para H substituent is sufficient.

A rationale consistent with these data and based on the earlier observations of Hanna and co-workers is shown in Scheme 3. Specifically, formation of the bis(aryloxide) complex Ar′Bi(OC$_6$H$_3{}^t$Bu$_2$-2,6)$_2$ (**A**) is conceivable, given that **6** can be formed. If this crowded complex **A** undergoes Bi−O bond homolysis as postulated in the literature[14] to form a bismuth radical (**B**) and the OC$_6$H$_3{}^t$Bu$_2$-2,6 radical (**C**), the latter species could rearrange to **D** and then be captured by **B**.

Following the rearrangement to **D**, the para C−H would now be adjacent to the aryloxide ligand in **E**. In the crowded environment enforced by the *tert*-butyl substituents, this could eliminate the observed HOC$_6$H$_3{}^t$Bu$_2$-2,6 byproduct and form **4**. Unexplained in this scheme is why **C** does not form radical coupling products as shown in Scheme 2 above. The specificity of this reaction and the high yield of **4** may be related to the efficiency of bismuth in the SOHIO process, namely, that in the proper coordination environment, bismuth can be very effective at C−H activation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Full experimental details; crystallographic collection data and selected metrical parameters for **2**−**6** (Tables S1−S4 and CIF); ORTEP drawings of the full asymmetric units for **3**, **4**, and **6** (Figures S1−S3); computational details; and calculated IR spectra for **4** and **5** (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 811909−811914 contain 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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