

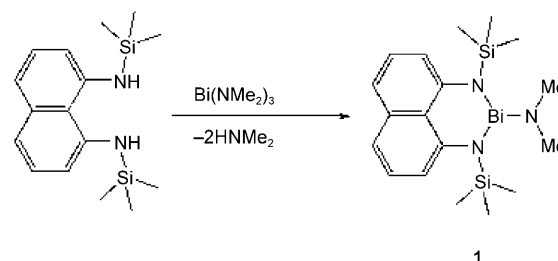
Addition of Dimethylaminobismuth to Aldehydes, Ketones, Alkenes, and Alkynes**

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Bismuth is a rare case of a nearly nontoxic heavy element that is used in medical applications.^[1] Nitrogen-containing compounds play an important role in many biologically active systems as well as in organic building blocks, new materials, and fine chemicals.^[2] Bismuth amido complexes are well established in main-group chemistry^[3] and we studied the beneficial influence of chelating N-ligands on the reactivity of bismuth some years ago.^[4] Related complexes have been proposed as key intermediates in important catalytic processes and especially in the fixation and activation of nitrogen.^[5] At the same time insertion reactions of carbonyl and alkene compounds into metal–nitrogen bonds have been known for lanthanides and for early and late transition metal complexes. However, the insertion of carbon–carbon and carbon–oxygen bonds into the metal–nitrogen bond has not been well studied with main-group compounds. This may be attributed to the poor reactivity of compounds with nitrogen bonds, although Ando et al. reported the reaction of bismuth amide with heterocumulenes.^[6] Lappert and co-workers described the addition of aminostannanes to a variety of alkynes and alkenes^[7] and also aminosilylation and aminophosphination reactions with highly electrophilic substrates.^[8] Recently Hartwig and co-workers reported transamination of alkenes and vinylarenes by rhodium(I) amides.^[9] The insertion of an alkyne into a molybdenum–amide bond has also been described.^[10] The work reported in this paper was fueled by the design and synthesis of main-group complexes with the focus on their reactivity toward insertion reactions.^[11] We report the syntheses and structural characterization of a bismuth amide complex and its reaction with aldehydes, ketones, alkenes, and alkynes.

The reaction of 1,8-bis[(trimethylsilyl)amino]naphthalene with $\text{Bi}(\text{NMe}_2)_3$ ^[12] led to the well-defined bismuth amide complex $[\text{1,8-C}_{10}\text{H}_6(\text{NSiMe}_3)_2\text{BiNMe}_2]$ (**1**) in good yield (Scheme 1).

Complex **1** is an orange solid, which is soluble in *n*-hexane, THF, and toluene and crystallizes in the monoclinic space



Scheme 1. Preparation of **1**.

group $P2_1/n$ with a trigonal pyramidal coordination geometry around the bismuth center (Figure 1).^[13] The N–Bi–N bond angles sum to 281.42° , and hence indicate that the stereochemically active lone pair is in the apical position. The Bi–N

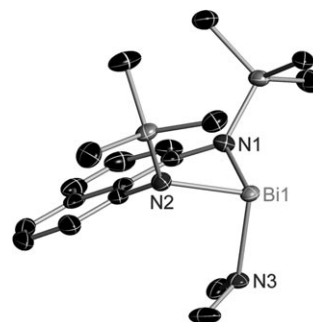


Figure 1. Crystal structure of **1**, with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi1–N1 2.150(1), Bi1–N2 2.176(1), Bi1–N3 2.179(1); N1–Bi1–N2 85.02(7), N1–Bi1–N3 100.06(7), N2–Bi1–N3 96.34(6).

bond lengths for **1** (average 2.168 Å) are comparable to those in structurally characterized $\text{Bi}(\text{NMe}_2)_3$.^[12] The ^1H NMR spectrum of **1** exhibits two singlets, at $\delta = 0.25$ and 2.48 ppm, for the SiMe_3 and NMe_2 groups, respectively.

The reaction of **1** with 2-benzoylpyridine proceeded smoothly at 25°C in *n*-hexane to give product **2** in 83% yield (Scheme 2). Complex **2** is monomeric in the solid state and crystallizes in the triclinic space group $P\bar{1}$ (Figure 2).^[13] The coordination environment around the bismuth atom is distorted trigonal pyramidal with bond angles in the range of $83.46(12)$ to $97.03(11)^\circ$ around the bismuth atom. The Bi–O bond length (2.089 (2) Å) is in the range of a Bi–O single bond when compared with other structurally characterized bismuth compounds.^[14] The Bi–N4 (donor side-arm) distance

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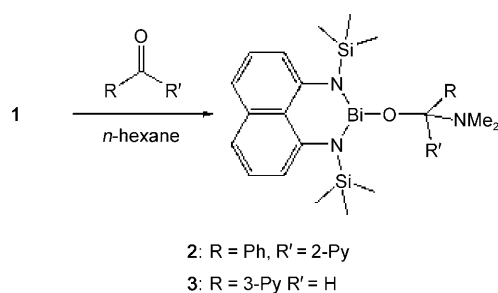
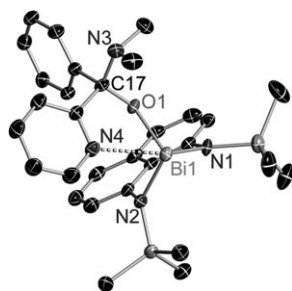
Scheme 2. Preparation of **2** and **3**.

Figure 2. Crystal structure of **2**, with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Bi1–O1 2.089(2), Bi1–N1 2.194(3), Bi1–N2 2.123(3), Bi1...N4 2.615(4), O1–C17 1.405(4); O1–Bi1–N1 85.44(11), O1–Bi1–N2 97.03(11), N1–Bi1–N2 83.46 (12), Bi1–O1–C17 125.4(2).

of 2.615(4) Å is considerably longer than the Bi–N bond lengths of the ligand (2.194(3) vs. 2.123(3) Å).

The ^1H and ^{13}C NMR spectra also indicate the formation of an addition product in which 2-benzoylpyridine is inserted into the Bi–N bond of **1** to form **2**. The ^1H NMR spectrum of **2** exhibits two different resonances, at $\delta = 0.47$ and 0.32 ppm, for the SiMe_3 groups and a singlet at $\delta = 1.59$ ppm for the NMe_2 substituent. The ^{13}C NMR spectrum of **2** shows an upfield-shifted carbonyl resonance, corresponding to the inserted ketone, which appears at $\delta = 94.8$ ppm ($\delta = 193.7$ ppm for the starting material).

In a similar manner, a *n*-hexane solution of **1** smoothly reacted with 3-pyridinecarboxaldehyde at room temperature to afford crystalline **3** in 75% yield (Scheme 2).

The characterization of **3** indicated that the insertion of 3-pyridinecarboxaldehyde occurred selectively into the Bi–N bond of **1**. Complex **3** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit and a trigonal pyramidal coordination environment around the bismuth atom with bond angles of 83.96(8) to 91.85(9)° (Figure 3).^[13] The Bi–O bond length in **3** (2.10(2) Å) is in the range of Bi–O single bonds in known examples (2.058 and 2.109 Å in $[\text{Bi}(\text{ONp})_3(\text{Py})_2]$).^[14] Also for this structure, the Bi–N4 distance (2.891(4) Å) is considerably longer than the Bi–N bond lengths of the ligand (2.170(2) and 2.164(2) Å).

The ^1H NMR spectrum of **3** exhibits singlet resonances for the dimethylamine and quaternary CH protons, at $\delta = 1.89$ and 5.05 ppm, respectively. The three methyl groups of the SiMe_3 ligands appear at $\delta = 0.3$ and 0.26 ppm. The ^{13}C NMR

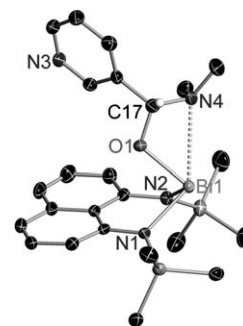
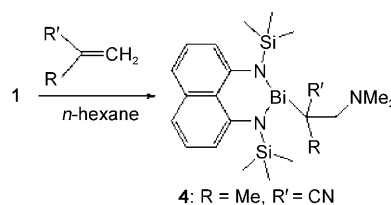


Figure 3. Crystal structure of **3**, with thermal ellipsoids set at 50% probability. Hydrogen atoms (except for those of C17) and disorder in one SiMe_3 group are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Bi1–O1 2.10(2), Bi1–N1 2.170(2), Bi1–N2 2.164(2), Bi...N4 2.891(4), O1–C17 1.388(4); O1–Bi1–N1 83.96(11), O1–Bi1–N2 91.85(9), N1–Bi1–N2 84.02 (9), Bi1–O1–C17 113.70(18)

spectrum of **3** shows a singlet resonance at $\delta = 89.23$ ppm, which can be assigned to the carbonyl group of the inserted aldehyde.

The driving force for the formation of compounds **2** and **3** is the formation of the Bi–O bond.^[15] Additionally, the intramolecular coordination between bismuth and nitrogen (Figures 2 and 3) may play an important role for the stability of these compounds. To extend these findings to bismuth–carbon bonds, we treated **1** with an alkene and an alkyne, while aware that the Bi–C bond is considerably weaker (143 kJ mol $^{-1}$)^[16] than the Bi–O bond. The reaction of **1** with 2-methyl-2-propenenitrile in *n*-hexane at 25°C gave the yellow complex **4** in 74% yield (Scheme 3). Like the other

Scheme 3. Preparation of **4**.

structures, **4** is monomeric in the solid state and crystallizes in the monoclinic space group $P2_1/c$. The bismuth atom in **4** again has the anticipated trigonal pyramidal coordination geometry. Moreover, the crystal structure of **4** reveals that the bismuth atom and the NMe_2 group are arranged on the same side of the molecule. This might be caused by the packing of the molecules in the crystal. The C17–C20 bond length of 1.540(5) Å is in the range of normal C–C single bonds (Figure 4).^[13]

The ^1H NMR spectrum of **4** shows two peaks corresponding to the non-equivalent CH protons of the methylene group ($\delta = 2.43$ and 4.53 ppm) and two singlets for NMe_2 and Me ($\delta = 2.08$ and 1.17 ppm). The ^{13}C NMR spectrum indicates the presence of a new resonance ($\delta = 62.6$ ppm), which can be assigned to the carbon atom that binds to the bismuth atom.

The reaction of **1** with diethyl acetylenedicarboxylate at 25°C in a 2:1 molar ratio resulted in the yellow product **5** in

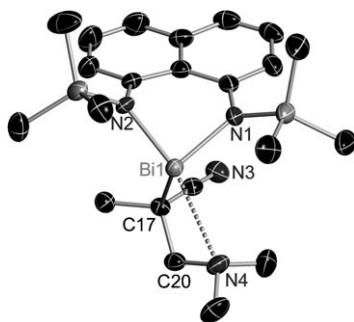
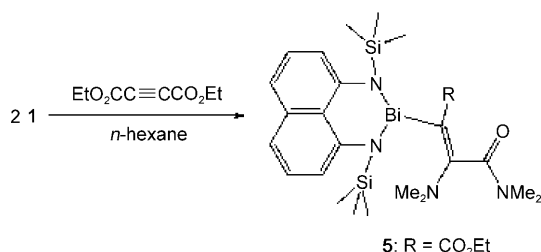


Figure 4. Crystal structure of **4**, with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Bi1–N1 2.171(3), Bi1–N2 2.155(3), Bi1–N3 2.936(6), Bi1–N4 2.341(3), N4–C20 1.462(5), C17–C20 1.540(5); N1–Bi1–C17 100.15(12), N2–Bi1–C17 94.37(12), N1–Bi1–N2 84.95(12), C20–C17–Bi1 100.5(2), N4–C20–C17 112.8(3).

55% yield (Scheme 4, Figure 5).^[13] Complex **5** is monomeric in the solid state and crystallizes in the triclinic space group $P\bar{1}$ with a trigonal pyramidal geometry at the bismuth atom. The



Scheme 4. Preparation of **5**.

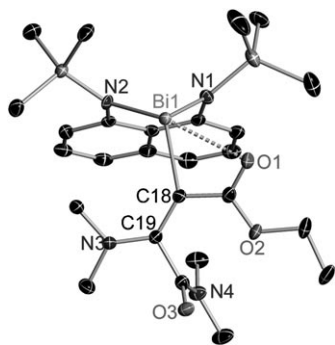


Figure 5. Crystal structure of **5**, with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Bi1–N1 2.178(3), Bi1–N2 2.20(30), Bi1–N3 2.70(40), Bi1–N4 2.29(8), C18–C19 1.381(5); N1–Bi1–C18 92.2(5), N2–Bi1–C18 103(6), N1–Bi1–N2 81.64(16).

structure reveals that the addition resulted in a *Z* orientation of bismuth and the amide relative to the double bond. The Bi–O1 (carbonyl O atom) distance (2.70(40) Å) is comparable with Bi–O_{carbonyl} distances in other known structures (2.56–2.86 Å).^[17]

Moreover, during the formation of **5** the exchange of one of the OEt groups with a NMe₂ substituent occurred. In the

¹³C NMR spectrum, the carbon atoms of the resulting C=C double bond in **5** resonate at δ = 169.3 and 174.4 ppm, respectively.

In summary, the chemistry described herein provides a facile and direct synthesis of substituted bismuth compounds in good yields with excellent regioselectivity. The chemistry shows easy formation of compounds incorporating Bi–O and Bi–C bonds. The reported synthesis is expected to be advantageously employed in organic and organometallic syntheses.

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[T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, 26, 615–619]. The structures were solved by direct methods (SHELXS) and refined on F^2 using the full-matrix least-squares methods of SHELXL [G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, 64, 112–120]. Cell parameters and R -values with $[I > 2\sigma(I)]$: **1**: space group $P2_1/n$; $a = 9.9870(9)$, $b = 12.5984(12)$, $c = 16.938(2)$ Å; $\beta = 93.3040(10)^\circ$; $wR2 = 0.0325$; $R1 = 0.0158$; **2**: space group $P\bar{1}$; $a = 9.597(2)$, $b = 9.836(2)$, $c = 17.485(3)$ Å; $\alpha = 74.10(3)$, $\beta = 82.87(3)$, $\gamma = 79.75(3)^\circ$; $wR2 = 0.0691$; $R1 = 0.0272$. **3**: space group $P\bar{1}$; $a = 10.8242(7)$, $b = 15.9185(10)$, $c = 16.6061(10)$ Å; $\alpha = 104.2030(10)$, $\beta = 92.2510(10)$, $\gamma = 96.9070(10)^\circ$; $wR2 = 0.0465$; $R1 = 0.0207$. **4**: space group $P2_1/c$; $a = 11.113(2)$, $b = 21.808(4)$, $c = 12.138(2)$ Å; $\beta = 114.36(3)^\circ$; $wR2 = 0.0494$; $R1 = 0.0249$. **5**: space group $P\bar{1}$; $a = 12.7227(14)$, $b = 13.3719(15)$, $c = 18.236(2)$ Å; $\alpha = 94.0560(17)$, $\beta =$

$91.5292(17)$, $\gamma = 98.822(2)^\circ$; $wR2 = 0.0671$; $R1 = 0.0270$. More details about the crystallographic data and the refinement can be found in the Supporting Information. CCDC 721257 (**1**), 717832 (**2**), 721258 (**3**), 717833 (**4**), and 721259 (**5**) 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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