Aminobismuthination of CO_2

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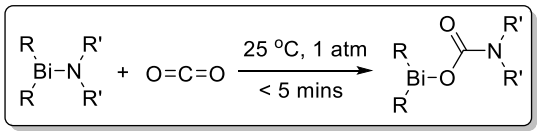
Abstract

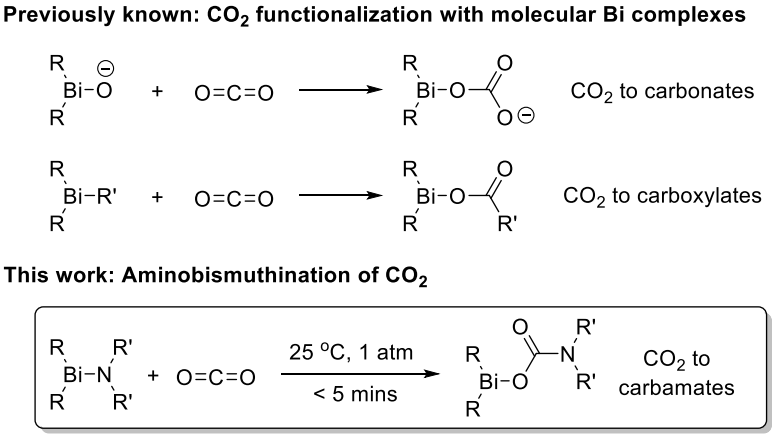
We report the facile (25 °C, 1 atm, <5 minutes) insertion of CO_2 into Bi-N bonds to yield rare examples of bismuth carbamates, whose structures show a μ_2-bridging mode that is hitherto unobserved in s, p, or f-block amide chemistry. The role of ligand and substituent on promoting the controlled aminobismuthination of CO_2 and rendering the bismuth carbamate products stable against thermal decomposition and ligand degradation is revealed.

TOC Graphic



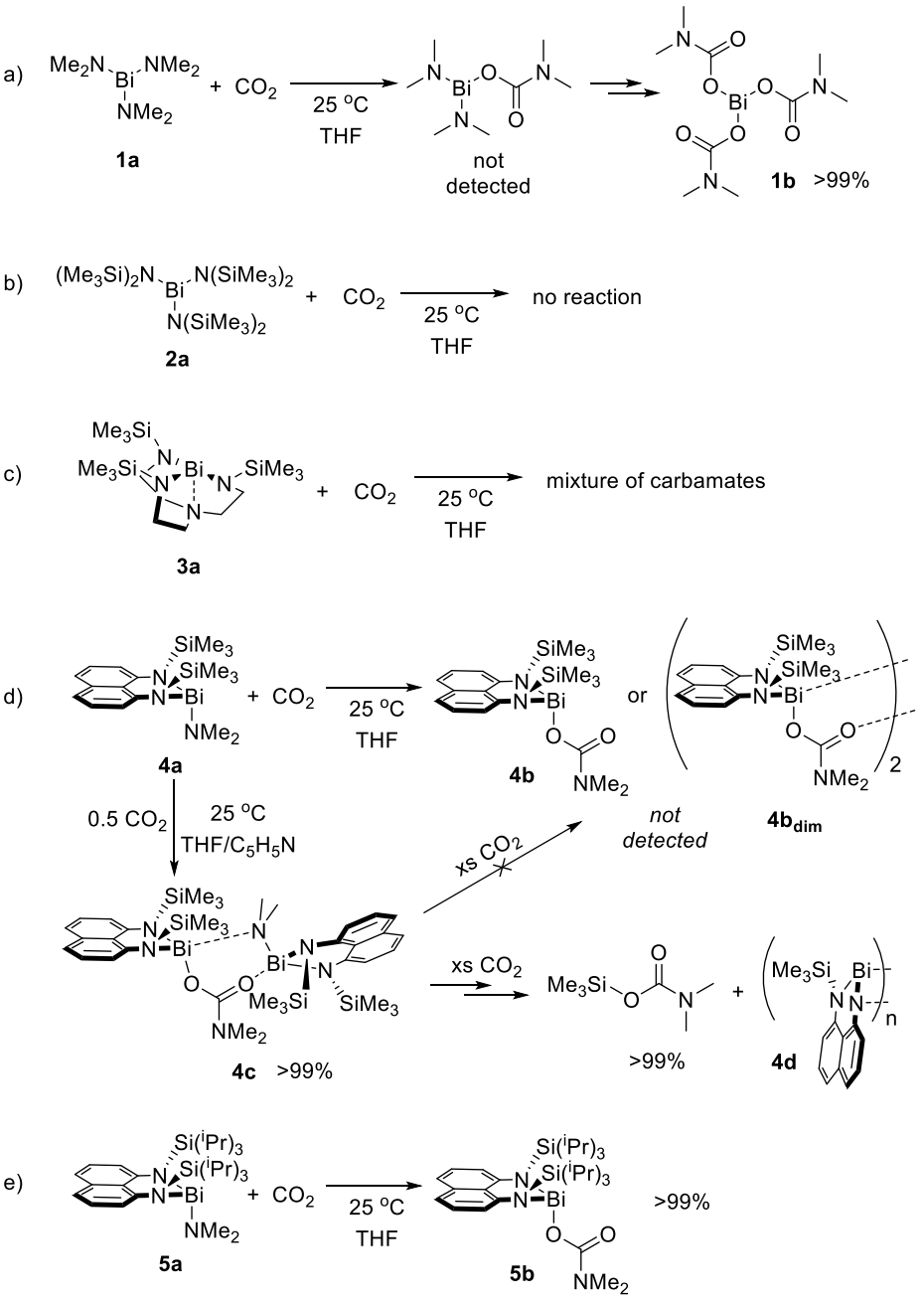
The capture and functionalization of CO_2 is at the heart of efforts to chemically valorize this potent green-house gas as a C_1 synthon.[1] Although the C=O bond is robust (ca. 500 kJ mol^{-1}),[2] its high polarity makes it kinetically susceptible towards reactions with strong dipoles. Metal amides — due to their very polar M-N bond, ready synthetic accessibility, and remarkable structural diversity — are therefore a bespoke platform for mediating the conversion of CO_2 to organic carbamates,[3] a class of compounds with applications in the synthesis of polymers,[4] insecticides,[5] and pharmaceuticals.[6]

In contrast to the facile insertion of CO_2 into the very polarized M-N bonds of electropositive s/d/f-block metal amides,[3, 7-10] uncatalyzed insertion into less polar heavy p-block M-N bonds is kinetically challenging, and has therefore been studied to a limited extent.[11-20] As part of our ongoing exploration into the electronic structure and reactivity of pnictogen amides,[21-26] we considered the potential for CO_2 activation with the heaviest family of such compounds — bismuth amides. Recent work showing that cationic and neutral bismuth amides can activate a host of challenging bonds established the prior plausibility of this endeavour.[27-30] The reaction of CO_2 molecule with Bi-O and Bi-C bonds is known to yield carbonates and carboxylates, respectively (Scheme 1, top).[31-36] In some instances, the captured CO_2 equivalent has been transferred to organic fragments (e.g. epoxides).[36, 37] To the best of our knowledge, however, aminobismuthination of CO_2 – addition of Bi-N bonds to CO_2 yielding carbamates (Scheme 1, bottom) – has not been definitively established, although spectral data suggests[38] it is viable. Bismuth carbamates are minimally-studied compounds with only one derivative characterized in the solid state, and it was made by an alkoxide/carbamate metathesis.[34]



Scheme 1. Conversion of CO_2 to carbonates, carboxylates and carbamates.

Here we report the facile aminobismuthination of CO_2 under ambient conditions (1 atm, 25 °C) with easily derivatized bismuth amides. The influence of amide basicity and ligand substitution upon the selectivity of CO_2 aminobismuthination is revealed, setting the stage for the future evolution of catalytic functionalization methodologies at well-defined molecular bismuth amides.



Scheme 2. Reactions of bismuth amides with CO_2 examined in this work. NMR yields given.

The homoleptic bismuth amide **1a** can in principle undergo single, double, or triple insertion of CO_2 and we envisioned the formation of complex mixtures. Instead, exposure of a yellow solution of **1a** to CO_2 instantly yielded the colourless tricarbamate **1b** (identified by comparison to known spectroscopic data)[38], irrespective of the amount of CO_2 supplied (Scheme 1a). For example, even when a 3:1 stoichiometry of **1a**:CO_2 was used, only unreacted **1a** and tricarbamate **1b** were observed by ^{1}H NMR spectroscopy, suggesting that the rate of the reaction increases as each NMe_2 group is replaced by O_2CNMe_2, resulting in the accumulation of the homoleptic derivative **1b**. Single crystals of the compound were obtained and examined by X-ray diffraction. While detailed discussion of metrical parameters is precluded by the degree of disorder, the data unambiguously establish the atomic connectivity, revealing a polymeric composition (Figure 1). The most notable feature is the μ_2 coordination which is the first example of such a binding mode for main group carbamates. A survey of the Cambridge Structural database further highlights the rarity of this bridging mode – only one other example is known across the periodic table in the form of a μ_2-bridged mixed iron oxide/carbamate cluster.[39]

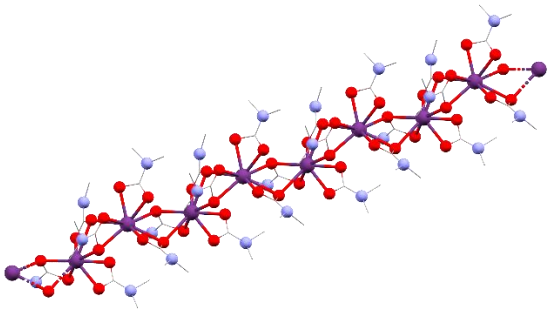


Figure 1. View of the polymeric structure of **1b** in the solid state. Hydrogen atoms have been omitted and carbon atoms shown in wireframe for clarity. A ball and stick representation is used because disorder in the diffraction data limited refinement to isotropic treatment.

The analogous reaction of $Bi(N(SiMe_3)_2)_3$ (**2a**) with CO_2 was unproductive as per ^{1}H NMR spectroscopy even after prolonged exposure to an excess of the gas (Scheme 1b). We hypothesized this was due to the greater steric bulk and lower basicity of the $N(SiMe_3)_2$ group relative to NMe_2 and considered triamide $N(CH_2CH_2N(SiMe_3))_3Bi$ (**3a**, Scheme 1c)[40] where both factors are addressed: the steric bulk is pinned back and one Me_3Si group is replaced by a methylene. Exposure of a yellow solution of **3a** to either limiting or excess CO_2 consistently

yields colourless solutions, but the complex mixture of species present in them have eluded definitive characterization, possibly due to oligomerization of the flexible ligand (broad CH_2 resonances observed in ^1H NMR spectra, Figure S1, Supporting Information). Nevertheless, the capture of CO_2 is unambiguously confirmed by IR spectroscopy analysis of the reaction mixtures, which show diagnostic C=O stretching frequencies in the 1450-1650 cm^{-1} range (Supporting Information).

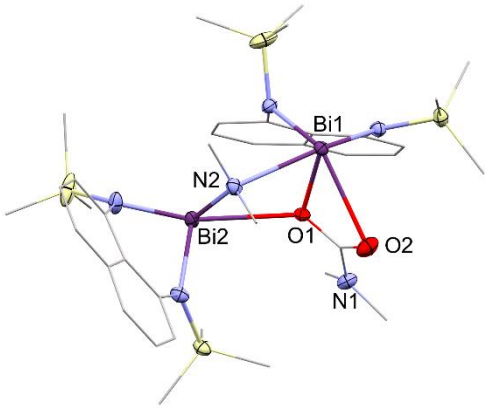


Figure 2. View of the structure of **4c** in the solid state. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are shown at the 50% probability level. One of two molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (°) are as follows: Bi1-O1 = 2.167(3), Bi1-O2 = 2.837(3), Bi1-N2 = 2.712(3), Bi2-N2 = 2.228(3), Bi1-N2-Bi2 = 103.83(1), Bi1-O1-Bi2 = 98.09(1).

To better control the selectivity of CO_2 aminobismuthination, compound **4a**[24, 41-43] was considered. Due to the greater basicity of alkylamides relative to arylamides and chelation enhanced stability of the Bi-N bonds involving the backbone, **4a** was expected to exhibit more defined reactivity and yield either **4b** or its dimer $\mathbf{4b_{dim}}$. Exposing an orange solution of **4a** to one equivalent of CO_2 instead led to the immediate formation of yellow **4c** in quantitative yield by ^1H NMR spectroscopy, confirming the selective addition of CO_2 to a single Bi-N bond. Crystals of the compound were obtained by slow cooling of a hexane solution, revealing a bimetallic structure where Bi1 hosts the carbamate in its primary coordination sphere and is five-coordinate due to interaction with both oxygen atoms [Bi1-O2 = 2.837(3) Å]. It is additionally coordinated to the NMe_2 moiety of an unreacted equivalent of **4a** [Bi1-N2 = 2.712(3)A, Bi2-N2

= 2.228(3) Å]. The carbamate substituent is again oriented in a manner that enables μ_2 binding to both metal centres [Bi1-O1 = 2.167(3) Å, Bi2-O1 = 2.928(3) Å].

Only one NMe_2 resonance, integrating to 12 protons, was detected for redissolved crystals of **4b** in benzene-d_6, tetrahydrofuran-d_8, or pyridine-d_5 at 300 K, suggesting a dynamic process that renders the two NMe_2 groups equivalent. Upon cooling down to the lowest temperature accessible to us (206 K), ^{1}H NMR spectroscopy in tetrahydrofuran-d_8 showed a downfield shift for the broad resonance and its partial resolution into two peaks, one of which overlaps with the broad resonance at each temperature point (Figure S2, Supporting Information). In parallel, the resonances of the aromatic and Me_3Si groups also show partial separation. These spectral changes being reversible as a function of temperature, we infer that their origins lie in a dynamic process that exchanges the metal-bound and carbamate-bound NMe_2 groups.

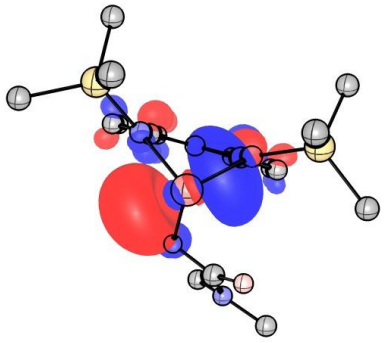


Figure 3. View of the LUMO of a monomeric version of **4c** at the PBE1/def2-svp level. Hydrogen atoms are omitted for clarity.

DFT calculations at the PBE1-D3/def2-svp level indicate the reaction of two equivalents of **4a** with CO_2 to give **4c** is exergonic by 37 kcal/mol (ΔG_{rxn} at 298 K, 1 atm). Conversion of **4c** to two equivalents of **4b** by addition of CO_2 is calculated to be thermoneutral (ΔG_{rxn} = 0.5 kcal mol^{-1}), but dimerization of **4b** to **4b$_{dim}$** is exergonic (ΔG_{rxn} = 13 kcal mol^{-1}). These values classify **4c** as an intermediate that should, in the presence of additional CO_2, spontaneously proceed to yield **4b$_{dim}$**, if kinetic barriers permit this reaction. In an attempt to observe such stoichiometric CO_2 insertion and thus access **4b** or **4b$_{dim}$** (or derivatives thereof), three strategies were tested.

First, precursor **4a** was exposed to CO_2 in pyridine as a strongly coordinating solvent to disrupt intermolecular association (required for formation of **4c**) and liberate free **4a** for further

reactivity with CO_2. However, this experiment also yielded **4c** as the exclusive product (Figure S3, Supporting Information) suggesting the pyridine cannot displace **4a** once **4c** is formed. DFT calculations show that the LUMO of the putative monomer **4b** is localized trans to one of the Bi-N bond, explaining its pronounced Lewis acidity (Figure 3), and further indicate that liberation of **4a** from this complex is substantially endergonic (19 kcal mol^{-1}).

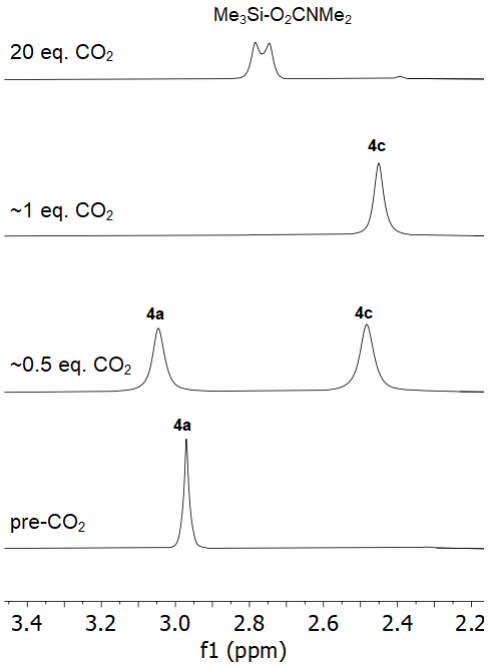


Figure 4. ^{1}H NMR spectra obtained upon successive additions of CO_2 to a solution of **4a** in pyridine-d_5.

To circumvent formation of **4b** entirely, we next treated a dilute solution of **4a** with a 10-fold excess of CO_2 to favour reactivity with the gas rather than a bimolecular process leading to **4b**. To our surprise, this experiment quantitatively yielded the silyl carbamate $Me_3Si\text{-}O_2CNMe_2$, indicating decomposition via N-Si bond scission (Figure 4 and Figure S4, Supporting Information). Mass balance and the anticipated reactivity of any unsaturated Bi=N bonds implicate **4d** or its oligomers as a possible by-product, although isolation of these decomposition products was not pursued.

Finally, we prepared compound **5a** featuring the bulky $Si(^iPr)_3$ groups to simultaneously thwart the formation of intermolecular adducts (e.g. **4c**) and shield the N-Si bond on steric grounds. Exposing **5a** to one equivalent of CO_2 resulted in the quantitative and rapid (< 5 minutes) formation of a single product (**5b**). Although the molecular structure of this species

could not be crystallographically determined, spectroscopic data strongly support its assignment as a monomeric bismuth carbamate. Specifically, a sharp NMe_2 resonance is observed (see SI) and ESI-MS spectra showed the highest mass peak at 754.4 m/z corresponding to loss of a single carbon atom. Moreover, attempts to optimize the geometry of the $Si(^iPr)_3$ derivatives of adduct **4c** or dimer $\mathbf{4b_{dim}}$ resulted in spontaneous dissociation into monometallic species. Crucially, addition of excess CO_2 also did not effect elimination of the silyl carbamate by N-Si bond breakage, further validating our steric protection hypothesis.

Given recent recognition that coordinating solvents (e.g. pyridine and tetrahydrofuran) can form transient solvent-CO_2 adducts, which are more reactive than gaseous CO_2 itself,[18] we sought to ascertain whether the formation of **4c** and **5b** was truly through reaction with the gas or instead with traceless solvent adducts. Therefore, solutions of **4a** in poorly-coordinating solvents 1,2-difluorobenzene or benzene were exposed to an equivalent of CO_2. In both cases, conversion to **4c** was observed, albeit more slowly due to the lower solubility of the gas in these media. We therefore infer that the observed reactivity arises from the direct reaction of Bi-N bonds with dissolved CO_2 rather than with a pre-activated solvent adduct.

In summary, we have provided the first definitive evidence for the aminobismuthination of CO_2, providing ready access to a minimally studied class of compounds – bismuth carbamates. Exerting control over this reaction required careful choice of ligand and substituents. Besides evidencing a rare class of molecules, the structures of **1b** and **4c** also provide the first example of the μ_2 bridging mode for the carbamate ligand in s, p, or f-block chemistry. Collectively, these findings of stoichiometric CO_2 aminobismuthination under mild conditions (1 atm, 25 ^oC) now motivate our pursuit of catalytic functionalization strategies to valorize this greenhouse gas using rationally designed bismuth amides.

Acknowledgments

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