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Carbon monoxide insertion at a heavy p-block element: unprecedented formation of a cationic bismuth carbamoyl†

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Major advances in the chemistry of 5th and 6th row heavy p-block element compounds have recently uncovered intriguing reactivity patterns towards small molecules such as H_2, CO_2, and ethylene. However, well-defined, homogeneous insertion reactions with carbon monoxide, one of the benchmark substrates in this field, have not been reported to date. We demonstrate here, that a cationic bismuth amide undergoes facile insertion of CO into the Bi–N bond under mild conditions. This approach grants direct access to the first cationic bismuth carbamoyl species. Its characterization by NMR, IR, and UV/vis spectroscopy, elemental analysis, single-crystal X-ray analysis, cyclic voltammetry, and DFT calculations revealed intriguing properties, such as a reversible electron transfer at the bismuth center and an absorption feature at 353 nm ascribed to a transition involving σ- and π-type orbitals of the bismuth-carbamoyl functionality. A combined experimental and theoretical approach provided insight into the mechanism of CO insertion. The substrate scope could be extended to isonitriles.

Introduction

The traditional distinction between transition metal and main-group compounds according to their physical and chemical properties has recently been challenged.[1] This is due to the fact that researchers are currently in the process of understanding how to design main group compounds with properties including a well-defined one-electron-redox chemistry, small HOMO–LUMO gaps of <4 eV, and remarkable reactivities in the activation of small molecules such as H_2, CO, CO_2, and ethylene.

Among the main group compounds, complexes of the heavy p-block elements with a principal quantum number of $n > 4$

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show some inherent characteristics with high potential for applications in synthesis and catalysis. These include low homolytic bond dissociation energies,[2] reversible homolytic bond cleavage/bond forming reactions,[3] and large ionic radii, which allow for the design of cationic species with a considerable soft Lewis acidity. In the case of bismuth, a relatively low toxicity of the element and its complexes should also be noted.[4] For compounds based on elements of the sixth row of the periodic table of the elements, relativistic effects come into play and may affect their physical and spectroscopic properties.[5]

When targeting highly reactive heavy main group species, low-valent compounds, complexes with element–element multiple bonds, and cationic species are promising candidates. However, the synthesis of such compounds may be extremely challenging. This is due to the inherent characteristics of heavy p-block elements, including (i) large ionic and covalent radii, which facilitate (unselective) oligomerization of low-valent species, (ii) relatively low redox potentials, which make over-reduction a serious synthetic problem, (iii) disproportionation reactions of mono-cationic complexes, and (iv) difficulties in accessing extremely Lewis-acidic and Lewis-basic species.

Despite these challenges, considerable efforts in designing heavy main group species that undergo well-defined reactions with small molecules have been crowned with success. The distannyne Sn_2Aryl_2 has been shown to reversibly add two equivalents of ethylene across its Sn≡Sn bond to give the corresponding distannane (Scheme 1a, Aryl = C_6H_3-2,6(C_6H_3-2,6-$iPr_2)_2$).[6,7] This distannyne and closely related derivatives also react with dihydrogen to give a dinuclear tin species with two

bridging hydride ligands, a reaction that has recently been shown to be reversible (Scheme 1b).[8] In an alternative strategy without any E–E multiple bonding, the hypervalent bismuth compound Bi(C$_6$H$_4$CH$_2$)$_2$NtBu(OMe) with one polar Bi–O bond has been shown to undergo reversible CO$_2$ fixation under mild reaction conditions (Scheme 1c).[9,10]

Apart from H$_2$, CO$_2$, and ethylene, carbon monoxide is an intriguing substrate for insertion chemistry, since it represents an attractive, versatile C1-building block in synthetic chemistry. Traditionally, its utilization for the synthesis of organic molecules such as alcohols, aldehydes, or carboxamides has been realized with transition metal carbonyl species acting as critical intermediates.[11] According to the Dewar–Chatt–Duncanson

model, the bond between CO and a transition metal constitutes of ligand-to-metal σ-donation and metal-to-ligand π-back-donation. It has been demonstrated that π-back-donation makes an important or even crucial contribution to the overall bonding energy of most synthetically relevant carbonyl compounds.[12] This renders carbon monoxide an extremely challenging substrate for compounds based on heavy p-block elements, because synthetically accessible species of this kind usually lack occupied orbitals of sufficient symmetry and energy for π-back-donation. As a result, insights in this field of research are very limited.[13,14] Electrochemical sensing of CO at SnO$_2$ or In$_2$O$_3$ surfaces at elevated temperatures has been related to the formation of carbonate and carboxylate species by IR spectroscopy.[15] Matrix isolation techniques allowed for the IR spectroscopic characterization of tin and lead carbonyl species such as SnCO, Sn(CO)$_2$, Sn$_n$CO, Pb$_n$CO, and SnCO$^-$ at 7–20 K (n = 1–4).[16] These reports have been complemented by additional purely theoretical studies on these and related compounds.[17] To the best of our knowledge, however, well-defined insertion reactions of carbon monoxide with compounds based on heavy p-block elements showing a principal quantum number of $n > 4$ have not been reported to date.

Cationic bismuth amides combine a considerable Lewis acidity with a good accessibility and a high reactivity, making them promising candidates for small molecule activation.[18–20] Insertion reactions with carbon monoxide in specific would grant direct access to cationic bismuth carbamoyls, an unprecedented structural motif with high potential for the stabilization of (intermediate) radical species (Scheme 1d).[21]

Here we demonstrate that a well-defined cationic bismuth amide undergoes highly selective and facile insertion reactions with carbon monoxide and isonitriles under mild conditions, yielding the first examples of cationic bismuth carbamoyls and amidinoyls, which were isolated and fully characterized.
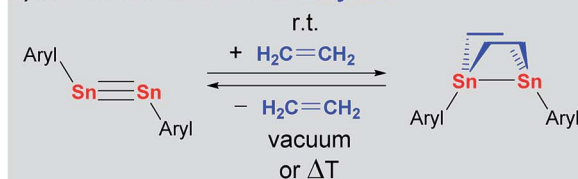
Results and discussion

The dinuclear cationic bismuth compound [Bi$_2$(N(C$_6$H$_4$)Ph)$_2$-(OTf)$_2$(thf)$_3$] (**1**) has recently been reported and was synthesized according to the literature (Scheme 2; Tf = SO$_2$CF$_3$).[19a,22] The prominent structural feature of compound **1** is a four-membered C$_2$NBi ring. The geometric parameters dictated by
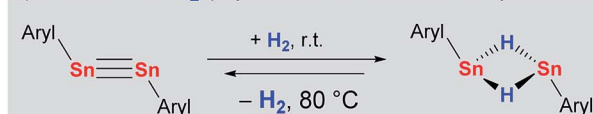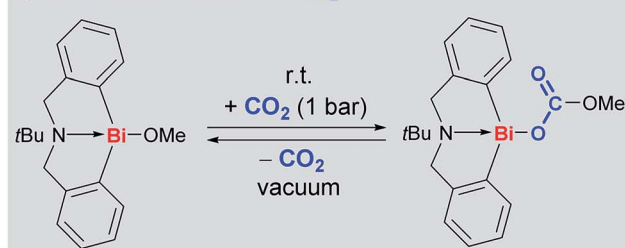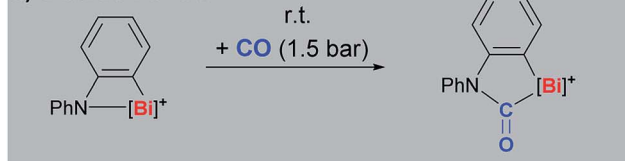

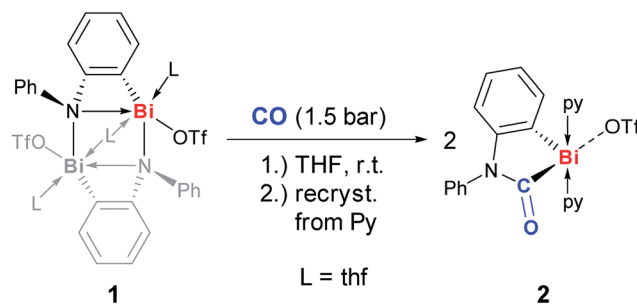**Scheme 1** Examples of well-defined compounds of heavy p-block elements that show unusual reactivity patterns towards small molecules. Aryl = C$_6$H$_3$-2,6(C$_6$H$_3$-2,6-iPr$_2$)$_2$.

Scheme 2 Insertion of CO into Bi–N bond of (masked) cationic bismuth amide **1** to give cationic bismuth carbamoyl compound **2**; py = pyridine, Tf = SO$_2$CF$_3$.

the phenylene unit suggest a considerable ring strain and lead to a significantly elongated Bi–N bond as part of the four-membered ring.[19] These characteristics seem predetermined for compound **1** to be highly active in small molecule activation reactions. Thus, compound **1** was reacted with carbon monoxide, which represents an extraordinarily challenging substrate in the chemistry of heavier group 15 compounds. When a suspension of yellow **1** in THF was exposed to an atmosphere of 1.5 bar CO the precipitation of a pale yellow solid indicated the consumption of the starting materials. Whereas a quantitative reaction monitoring by IR and NMR spectroscopy was hampered by the moderate to poor solubility of the starting material and the product in THF, these methods still indicated significant conversion of **1** after 1 h. However, extended reaction times of 2 d were necessary to reach full conversion of **1**, which was otherwise difficult to separate from the product. Recrystallization of the crude precipitate from pyridine/Et$_2$O/pentane gave the insertion product **2** in 61% yield (Scheme 2).[23] Compound **2** is moderately soluble in THF, but adequately soluble in pyridine. In pyridine solution, it is stable at ambient temperature and under ambient lighting for at least five weeks and at 80 °C for at least 2 h. NMR spectroscopy indicated the substitutional lability of the pyridine ligands, which can be removed *in vacuo* at 80 °C. ^{1}H and ^{13}C and ^{19}F NMR spectroscopic analyses revealed the expected signal patterns for the functional groups present in **2** (a phenylene and a phenyl group, two pyridine ligands, and a triflate). An unusually large ^{13}C NMR chemical shift of 251 ppm was recorded for the *C*ONR$_2$ group, which was ascribed to its interaction with the Lewis acidic cationic bismuth center.[24] IR spectroscopic analyses revealed a CO stretching frequency of 1637 cm^{-1} for the carbamoyl functional group. This is close to those reported for carbamoyl compounds of Sn and Pb, which were prepared by classical salt elimination protocols.[25]

The molecular structure of **2** was unambiguously identified by single-crystal X-ray diffraction (monoclinic space group $P2_1/n$ with $Z = 4$; Fig. 1). This confirmed the insertion of CO into the former Bi–N bond, resulting in formation of a bismuth carbamoyl moiety, an unprecedented structural motif.[26] The Bi1–C13 bond is considerably longer than the Bi1–C2 bond ($\Delta = +0.11$ Å). Despite the cationic nature of **2**,[22] the Bi–(CONR$_2$) bond length is in the same range as that of electronically stabilized Bi–C bonds in neutral compounds such as Bi(CH(SiMe$_3$)$_2$)$_3$, Bi(η^1-2-Me-allyl)$_3$, or Bi(CF$_2$CF$_3$)$_3$.[27] Accordingly, the C13–N1 distance of 1.38 Å is in agreement with a partial C=N double bond character. According to an energy decomposition analysis (EDA) of **2** and related species, these differences in Bi–C bond lengths are also reflected by the corresponding interaction energies: in homolytic bond dissociations, the interaction energy of the Bi–Aryl bond is 17.9 kcal mol^{-1} larger than that of the Bi–CONR$_2$ bond (ESI†). The covalent character of both types of bonds amounts to 44–49% according to EDA. In the solid state, **2** forms a loosely associated contact ion pair. The Bi1⋯O2 distance of 3.16 Å is 12% below the sum of the van-der-Waals radii, but significantly elongated compared to the Bi–OTf bond of 2.37 Å in starting material **1**.[19a] The coordination geometry around the bismuth center in **2** is saturated by two
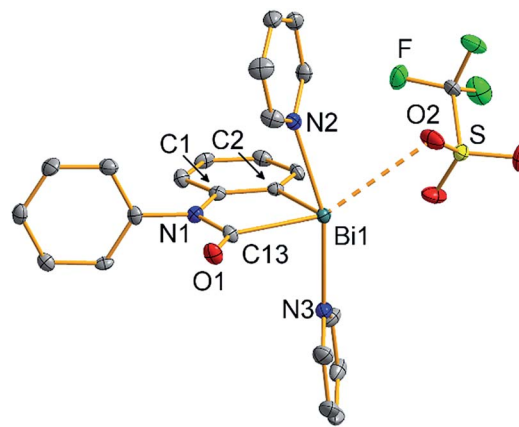

Fig. 1 Molecular structure of [Bi(CONPh(C$_6$H$_4$))(NC$_5$H$_5$)$_2$][OTf] (**2**) in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi1–C2, 2.227(5); Bi1–C13, 2.335(5); Bi1–N2, 2.520(4); Bi1–N3, 2.471(4); Bi1⋯O2, 3.164(4); C13–O1, 1.213(5); C13–N1, 1.382(6); C2–Bi1–C13, 76.60(16); C2–Bi1–N2, 84.21(15); C2–Bi1⋯O2, 103.25(14); N2–Bi1–N3, 163.56(13); C13–Bi1⋯O2, 153.50(14); $\tau_5 = 0.17$.

pyridine ligands in *trans*-position to each other. Overall, this results in a distorted square pyramidal coordination geometry around bismuth with C2 in the apical position ($\tau_5 = 0.17$).[28]

The electrochemical behavior of **2** was investigated by cyclic voltammetry in THF/0.1 M [N(nBu)$_4$][PF$_6$] at 23 °C, which revealed a chemically reversible redox event at an only moderately negative potential of −1.66 V *vs.* Fc/Fc$^+$ (Fig. 2a and ESI;† Fc = Fe(C$_5$H$_5$)$_2$). According to DFT calculations, the radical generated upon reduction is free of neutral donor ligands, [Bi(CONPh(C$_6$H$_4$))]$^\bullet$ (**2red**). 74% of the spin density are located at the bismuth center, occupying a molecular orbital with dominating contributions from a Bi-6p-type atomic orbital (Fig. 2b and ESI†). The remaining spin density is delocalized over the phenylene and the carbamoyl unit of **2red**, with spin densities of up to 5% at single C, N, and O atoms. This delocalization of spin density is believed to contribute to the stability of this species under the conditions of the
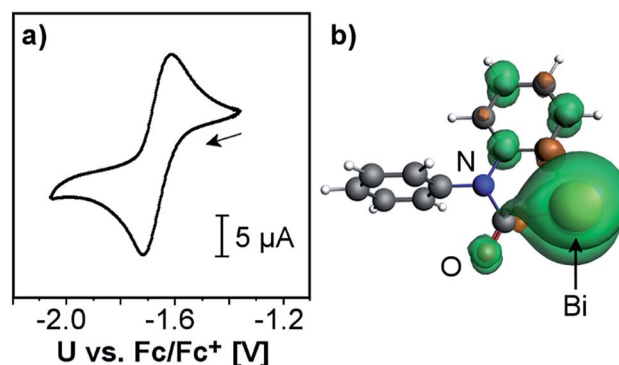

Fig. 2 (a) Cyclic voltammogram of **2** in THF/0.1 M [N(nBu)$_4$][PF$_6$] at 23 °C with a scan rate of 500 mV s^{-1}; Fc = Fe(C$_5$H$_5$)$_2$. (b) Optimized geometry and spin density distribution (iso value = 0.001) of reduced species [Bi(CONPh(C$_6$H$_4$))]$^\bullet$ (**2red**).

electrochemical experiment. While two examples of isolable Bi[II] radical species and one example of a persistent Bi[II] radical species have recently been reported,[3a,29] this is the first example of a quasi-reversible electron transfer at a mononuclear bismuth compound with the bismuth atom being the major spin carrier, demonstrating the potential of the bismuth carbamoyl functional group for the stabilization of (intermediate) radical species.[30] The pale yellow compound **2** was further investigated by UV/vis spectroscopy in THF solution, which revealed a broad absorption band at $\lambda_{max} = 353$ nm (FWHM = 96 nm; Fig. 3). In dilute solutions, the substitutionally labile

pyridine ligands of **2** can presumably be exchanged for thf ligands (ESI†). TD-DFT calculations at the CAMY-B3LYP/TZ2P level of theory on $[Bi(CONPh(C_6H_4))(thf)_2]^+$ indicated a HOMO−1/LUMO singlet–singlet transition at $\lambda = 354$ nm, when spin–orbit-coupling was taken into account using perturbation theory (for details see ESI†). This transition is suggested to correspond to the experimentally observed band at $\lambda_{max} = 353$ nm. The HOMO−1 shows major contributions by orbitals forming the Bi–C and C–N σ-bonds in the carbamoyl group and by an oxygen-centered p-type orbital. The LUMO consists of a bismuth-centered p-orbital and the π*-orbital of the CO group, both of which are orthogonal to the plane defined by the carbamoyl functionality. Thus, the bismuth carbamoyl functional group is directly involved in the electronic transition that is triggered by light in the UV/vis region ($\lambda \approx 310$–400 nm).

The mechanism of CO insertion was investigated by DFT calculations (Scheme 3, for details see ESI†).[31] All values are given in kcal mol^{-1}. We suggest coordination of CO to a Lewis-acidic bismuth center to be the initiating reaction step leading to intermediate **I-1** (ΔH: +9.7; ΔG: +5.9).[32] Insertion of the CO molecule proceeds *via* transition state **TS-1**, in which the CO unit bridges a Bi and an N atom (barrier: $\Delta H^{\neq}$: +8.5; $\Delta G^{\neq}$: +10.5), to give intermediate **I-2** in an almost thermoneutral reaction (ΔH: +0.2; ΔG: +3.0). A similar sequence of CO-coordination (to give **I-3**) and formation of a transition state with a Bi⋯(CO)⋯N unit (**TS-2**, barrier: $\Delta H^{\neq}$: +9.3; $\Delta G^{\neq}$: +11.6) and insertion leads to dinuclear intermediate **I-4**. Coordination of THF gives the monomeric compound **I-5**, which is suggested to be the species that precipitates from the reaction mixture, when **1** is reacted with CO in THF (*vide supra*).[23] Up to this point the overall reaction is exothermic and endergonic according to
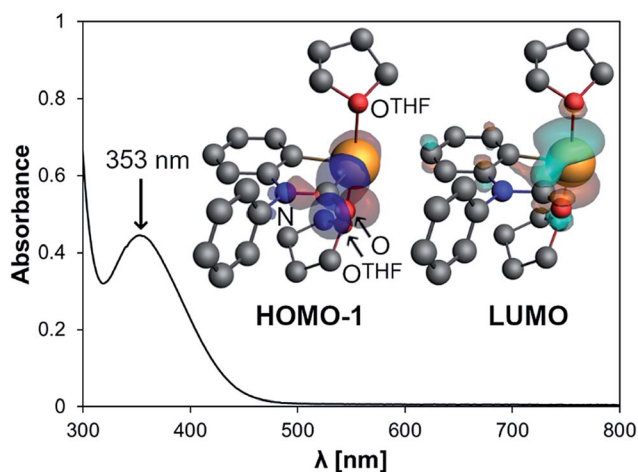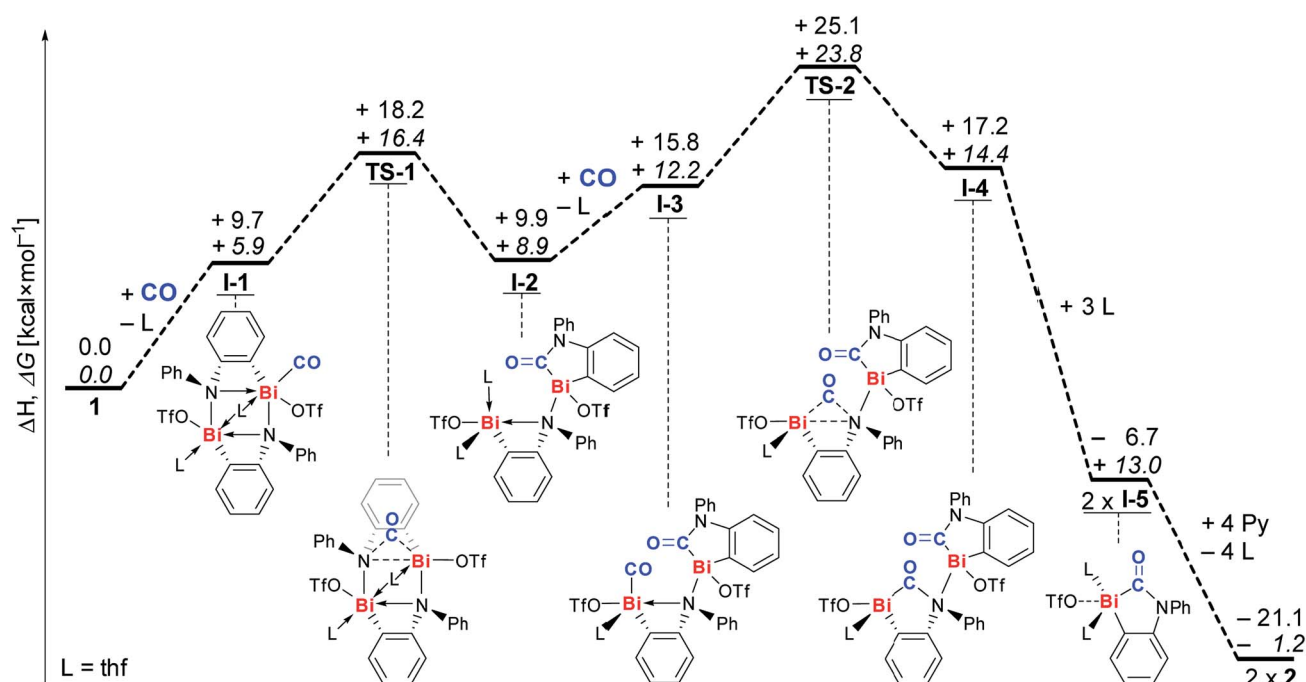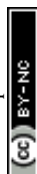

Fig. 3 UV/vis spectrum of **2** (0.4 mM solution in THF) and orbitals involved in the transition at 353 nm according to TD-DFT calculations on $[Bi(CONPh(C_6H_4))(thf)_2]^+$.


Scheme 3 Proposed mechanism for reaction of **1** with CO to give insertion product **2**; ΔH values (regular font) and ΔG values (italic) are given in kcal mol^{-1}. L = thf.

DFT calculations (ΔH: −6.7; ΔG: +13.0), and the formation of **I-5** is presumably aided by its poor solubility in THF. The exchange of THF for pyridine ligands to give isolated product **2** is exothermal and exergonic, reflecting the Lewis acidity of the bismuth atom (ΔH: −14.4; ΔG: −14.2). Monitoring the reaction by IR spectroscopy indicated the accumulation of **I-5** in solution until its saturation concentration was reached (characteristic band at 1592 cm^{-1}).[23] Whereas intermediates **I-1**, **I-2**, and **I-3** could not unambiguously be identified due to their low concentrations, signal overlapping, or their short-lived character, bands at 1655 and 1669 cm^{-1} were tentatively assigned to intermediate **I-4** (ESI†).

Putting the unusual reactivity of **1** towards carbon monoxide into the broader context of main group chemistry reveals some remarkable points. Compounds of strongly electropositive elements of Groups 1 and 2, as well as light(er) elements of Group 13 (B–Ga) undergo insertion with CO; examples include species such as nBuLi, LiN(iPr)$_2$, MgEtBr, or Al(tBu)$_3$.[33,34] These reactivity patterns may be interpreted as a result of the strong polarization of the M–X bond (X = C, N) and the high Lewis acidity of the main-group compound. In addition, compounds of Group 13 and 14 elements with low-valent character or with E–E (single or multiple) bonds have been reported to undergo intriguing insertion reactions with carbon monoxide (E = Group 13/14 element). Examples include diborynes, diboracumulenes, carbenes, germylenes and a disila-Dewarbenzene.[35–37] When it comes to well-defined compounds of the pnictogens P–Bi, selective insertion reactions with CO under mild conditions have only been reported for phosphorous species. Two different strategies have been reported in this context. Frustrated Lewis pairs (FLPs) with a phosphane moiety as the Lewis basic component react with CO under mild conditions to form heterocyclic compounds.[38–43] The second strategy exploits the reactivity of a phosphorus biradicaloid, which inserts CO under harsher conditions to give a P$_2$N$_2$C ring motif that maintains the biradicaloid character.[44] Overall, compound **1** represents the first molecular heavy p-block compound ($n > 4$) to undergo a direct and well-defined insertion reaction with carbon monoxide under mild conditions. The Lewis acidity and geometric constraints of **1** play key roles in determining its remarkable reactivity. It may be considered to interpret these driving forces in terms of FLP chemistry with a Lewis basic N and a Lewis acidic Bi site.[45c,d] To the best of our knowledge, this would be the first example of FLP chemistry of molecular compounds being extended to the heavy main group element bismuth.[45–47]

In order to extend the scope of the unusual insertion reactions of **1** with unsaturated small molecules, isonitriles were targeted due to their isoelectronic and isolobal relationship with carbon monoxide. Well-defined insertion reactions of pnictogen compounds with isonitriles are rare. Transition metal-stabilized phosphinidenes and arsinidenes [E(C$_5$Me$_5$)-(W(CO)$_5$)$_2$] (E = P, As) have been reported to coordinate sterically demanding C≡NtBu and to undergo insertion reactions with less bulky isonitriles C≡NR (R = $cyclo$-hexyl, nBu).[48] Only recently, the first example of an insertion reaction between a bismuth compound and an isonitrile has been documented:
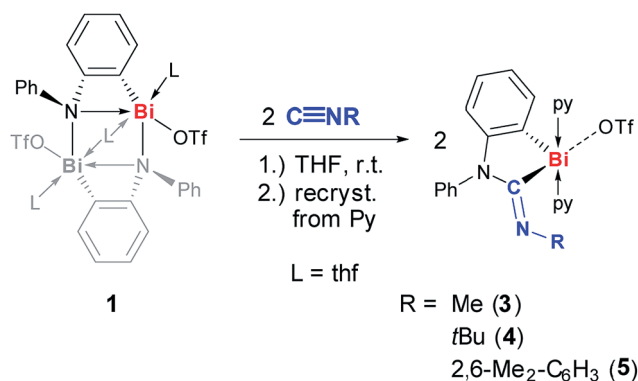
Scheme 4 Insertion of C≡NR into Bi–N bond of (masked) cationic bismuth amide **1** to give cationic bismuth amidinoyl compounds **3**, **4**, and **5**; py = pyridine, Tf = SO$_2$CF$_3$.
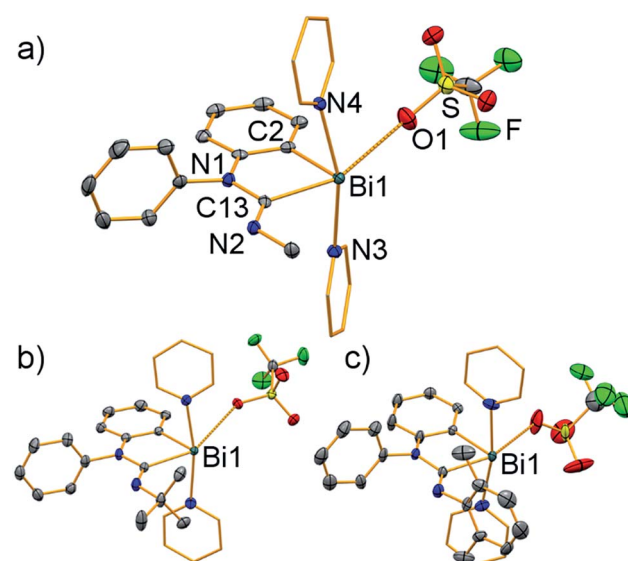

Fig. 4 Molecular structures of [Bi(CNRNPh(C$_6$H$_4$))(NC$_5$H$_5$)$_2$][OTf] in the solid state ((a) **3** (R = Me); (b) **4** (R = tBu); (c) **5** (R = 2,6-Me$_2$-C$_6$H$_3$)). Displacement ellipsoids are shown at the 50% probability level; carbon atoms of pyridine ligands are shown as wireframe for clarity. Hydrogen atoms, lattice-bound solvent molecules, and split positions of disordered groups in (c) are omitted for clarity. Atom labelling in (b) and (c) is in analogy with that in (a). Selected bond lengths (Å) and angles (°): (a) Bi1–C2, 2.222(3); Bi1–C13, 2.305(3); Bi1–N3, 2.499(2); Bi1–N4, 2.482(2); Bi1⋯O1, 3.025(2); C13–N1, 1.402(3); C13–N2, 1.263(3); C2–Bi1–C13, 76.84(10); C2–Bi1–N3, 84.48(8); C2–Bi1⋯O1, 79.86(9); N3–Bi1–N4, 164.35(7); C13–Bi1⋯O1, 155.56(8); τ_5 = 0.15. (b) Bi1–C2, 2.225(3); Bi1–C13, 2.331(3); Bi1–N3, 2.485(3); Bi1–N4, 2.525(3); Bi1⋯O1, 2.997(2); C13–N1, 1.415(4); C13–N2, 1.261(4); C2–Bi1–C13, 77.35(12); C2–Bi1–N3, 87.63(11); C2–Bi1⋯O1, 80.94(10); N3–Bi1–N4, 169.39(9); C13–Bi1⋯O1, 153.18(9); τ_5 = 0.27. (c) Bi1–C2, 2.202(4); Bi1–C13, 2.299(4); Bi1–N3, 2.510(4); Bi1–N4, 2.488(4); Bi1⋯O1, 2.907(15); C13–N1, 1.43(2); C13–N2, 1.269(6); C2–Bi1–C13, 76.89(15); C2–Bi1–N3, 84.96(14); N3–Bi1–N4, 169.41(13); C13–Bi1⋯O1, 158.8(3); τ_5 = 0.18.

the strongly nucleophilic nature of the boryl group in [Ph$_2$-Bi(BR$_2$)] allowed for isolation of the insertion product [Ph$_2$-Bi(C(NPh)BR$_2$)] in 22% yield, when C≡NPh was used as the substrate (BR$_2$ = 1,2,4,3-triazaborol-3-yl).[49] Remarkably, the

alkyl isonitrile C≡N(nBu) was found to undergo fragmentation with formation of [BiPh$_2$(nBu)], implying that isonitrile insertion is not a general reaction pathway for this bismuth boryl compound.

At ambient temperature, compound **1** readily reacted with isonitriles, C≡NR, that bear alkyl or aryl substituents with a steric profile varying from extremely low (R = Me) to high (R = tBu, 2,6-Me$_2$-C$_6$H$_3$) (Scheme 4). Monitoring the reaction by ^{1}H-NMR spectroscopy in the case of R = tBu revealed full conversion within 10 min and a high spectroscopic yield of >95%. The insertion products **3–5** were isolated in 60–79% yield after recrystallization from pyridine and fully characterized (Scheme 4, Fig. 4). In all cases the bismuth amidinoyl moiety was exclusively formed in its *Z*-configuration according to NMR spectroscopy. Compounds **3–5** show ^{13}C NMR chemical shifts between 210 and 223 ppm and IR bands at 1606–1637 cm^{-1} for the *C*NRNR$_2$ functionality.

Single-crystal X-ray diffraction analyses revealed a very similar coordination behavior for compounds **3–5** (Fig. 4). In each case, the bismuth atom is found in distorted square pyramidal coordination geometry with C2 in the apical position (τ_5 = 0.15–0.27). The Bi–C distances of the amidinoyl unit (Bi1–C13, 2.30–2.33 Å) are significantly larger than those involving the aryl group (Bi1–C2, 2.20–2.23 Å). The N1–C13 bond lengths of 1.40–1.43 Å suggest partial double bond character, albeit they are larger than those in carbamoyl compound **2** (1.38 Å).

Conclusions

In summary, we have reported the facile insertion of carbon monoxide into a bismuth–nitrogen bond, exploiting the Lewis acidity of the cationic bismuth compound and the release of ring strain as driving forces of the reaction. To the best of our knowledge, this is the first example of a molecular compound based on a heavy p-block element with the principal quantum number $n > 4$ to undergo a well-defined insertion reaction with carbon monoxide under mild conditions. This grants access to a novel cationic bismuth carbamoyl species, which allows for the first time to realize a chemically reversible redox process at the bismuth center of a mononuclear molecular compound. The pale yellow color of this compound was attributed to a singlet-singlet-transition that involves the bismuth carbamoyl functionality and is facilitated by spin–orbit coupling. Isonitriles were shown to analogously undergo these unusual insertion reactions. These results reveal the potential of heavy main group compounds in small-molecule activation, reversible electron–transfer reactions at heavy main group elements, and photochemistry targeting the accessibility of excited states with visible light.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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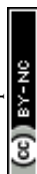
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