Catalytic Activation of N₂O at a Low-Valent Bismuth Redox Platform

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Herein we present the catalytic activation of N₂O at a Bi²⁺⇄Bi³⁺ redox platform. The activation of such a kinetically inert molecule was achieved by the use of bismuthinidene catalysts, aided by HBpin as reducing agent. The protocol features remarkably mild conditions (25 °C, 1 bar N₂O), together with high turnover numbers (TON, up to 6700) and turnover frequencies (TOF). Analysis of the elementary steps enabled structural characterization of catalytically relevant intermediates after O-insertion, namely a rare arylbismuth oxo dimer and a unique monomeric arylbismuth hydroxide. This protocol represents a distinctive example of a main-group redox cycling for the catalytic activation of N₂O.

Nitrous oxide (N₂O) is known to be a potent greenhouse gas, with much greater warming potential than CO₂.¹ The concentration of this gaseous molecule in the atmosphere has significantly increased in the modern era as a result of human activities, thus generating an environmental threat.¹b In this sense, the development of catalytic strategies for the decomposition of N₂O has recently drawn much attention.² From the chemical standpoint, N₂O is a thermodynamically powerful O atom transfer reagent, and indeed, Nature has evolved a powerful enzymatic pathway for converting N₂O into N₂ in microbial denitrification processes.³ Yet, N₂O is kinetically inert, which poses challenges for its catalytic activation with artificial systems.²c In contrast to heterogeneous catalysts,²a,b,d a handful of examples are known to be capable of activating N₂O based on homogeneous catalysts (Figure 1A),²e mainly consisting of transition metals (Ru,⁴ Rh,⁵ Co,⁶ and others⁷).

With the aim of emulating transition-metal-like reactivity, a growing number of organo-main-group compounds have been shown to activate small molecules.⁸ Among them, many low-valent p-block compounds circumvented the kinetic barrier for N₂O activation and formed structurally unique O-containing compounds.⁹ Additionally, frustrated Lewis pairs (FLPs)¹⁰ and N-heterocyclic carbenes (NHCs)¹¹ have also been shown to capture N₂O and eventually cleave the N−O bond. Recently, degradation of N₂O with disilanes initiated by a fluoride anion has also been achieved,¹² representing alternative pathways based on main-group systems. However, despite these precedents, catalytic redox processes for the activation of N₂O by a main group compound still remain elusive.

Based on earlier precedents, activation of N₂O could be facilitated by low-valent main group species, through the formation of an M−O bond with release of N₂.⁹ If catalytic turnover is to be achieved, such M−O species should be reduced satisfactorily back to the starting low-valent main group catalyst. Although this process is well-established for high-valent oxo compounds,¹³ access to low-valent counterparts is nontrivial. Nevertheless, bismuth presents itself as an interesting candidate to address such a challenging idea, due to its demonstrated ability to access various oxidation states.¹⁴ One-electron Bi²⁺⇄Bi³⁺ has been described by Coles¹⁵ and recently by Lichtenberg,¹⁶ whereas, two-electron Bi redox catalysis (Bi¹⁺⇄Bi³⁺ and Bi¹⁻⇄Bi¹⁺) has recently been reported by us.¹⁷−¹⁹ We have previously demonstrated that the N,C,N-chelated bismuthinidene complexes, originally reported by Dostál,²⁰ provide a privileged platform for Bi¹⁺⇄Bi¹⁺ redox cycles.²¹

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cycling. Herein, we demonstrate that $N_C N$-chelated bismuthinidines are able to catalyze $N_2 O$ deoxygenation in the presence of pinacolborane (HBpin) (Figure 1B). The catalytic system features the activation of $N_2 O$ at remarkably mild conditions (25 °C, 1 bar) with high TON (up to 6700) and TOF. Ligand design and structural analysis on the bismuthinidene catalyst enabled the full characterization of key $\text{Bi}^{15}$-oxo intermediates by NMR, X-ray, and HRMS.

To interrogate the reactivity of bismuthinidines with $N_2 O$, we initially subjected complex 1 to a $N_2 O$ atmosphere (1 bar) in THF-$d_8$ at −78 °C (Scheme 1). The green solution slowly turned pale yellow with concomitant evolution of gas. Analysis of the head space by GC-TCD identified the formation of $N_2$ during the reaction.$^{21}$ $^1H$ NMR analysis at −40 °C revealed complete consumption of 1 after 45 min and the formation of a major species containing intact $N_C N$-ligand scaffold and a $\text{C} = \text{Bi}$ bond.$^{21}$ ESI-HRMS analysis of this mixture clearly suggested the formation of dimeric arylbismuth oxides [{[ArBiO]}$_2$]+$^{+}$, calcld 937.33012, found 937.33070]. Such species was found to be dynamic in solution and thermally unstable, preventing its characterization by crystallographic techniques. The observed behavior for this species is consistent with other related Ar$–\text{Bi}^{15}$ oxo or sulfo dimers.$^{22}$

In order to shed light on the possible structure of this species, the $tBu$ on imines was replaced with $m$-terphenyl ($m$-Tp, 4 and 5, Figure 2A), which has been previously utilized to stabilize reactive organobismuth compounds such as Bi−H$^{25}$ and Bi−OH.$^{27}$ Due to the sensitivity of ary-$(\text{ket})$imines to metal hydrides,$^{28}$ we developed a facile and scalable procedure to obtain 4 and 5: reduction of the parent arylbismuth dichlorides 2 and 3 with $\text{Cp}_2\text{Co}$ afforded 4 and 5 after simple filtration as dark purple and red-purple solids respectively in very high yields (Figure 2B)$^{21}$ X-ray crystallography revealed that, in spite of the steric bulkiness of the $m$-Tp groups, the bond lengths and angles resemble those reported for 1 and related ketimine-$N_C N$-complexes of bismuth (Figure 2B)$^{20}$.

When 4 was exposed to a $N_2 O$ atmosphere at room temperature, the color slowly changed from dark purple to pale yellow and evolution of $N_2$ was observed (Figure 3A). $^1H$ NMR analysis at −50 °C confirmed the full consumption of 4 after 40 min and indicated the formation of a single species with an asymmetric $N_C N$-pincer backbone. Crystals suitable for X-ray crystallography were obtained by slow diffusion of $n$-pentane into a concentrated toluene solution of the reaction mixture at −78 °C. The crystal structure unequivocally determined the presence of the dimeric mono-organobismuth oxide 6, which features two $\mu$-oxo bridge moieties (Figure 3B).

Examples of mono-organobismuth(III) oxides are rare.$^{22,23,29}$ Due to the high polarity of the Bi−O bond and the large difference in orbital size between Bi and O, these oxides readily undergo dimerization or polymerization.$^{30}$ To the best of our knowledge, only two crystal structures of dimeric mono-organobismuth oxides have been reported: a...
Here, 6 represents an anti-isomer with a slightly asymmetric $\text{Bi}_2\text{O}_2$ core (Figure 3B). As a result of the weak coordination of N1 to Bi1 [Bi1–N1, 2.672(4) Å], the Bi1–O2 distance [2.120(3) Å] is marginally longer than Bi1–O1 [2.103(3) Å]. Interestingly, one m-Tp group in each half of the complex points away from the central Bi.

Although H27 could not be refined unambiguously, the short C27–O2 distance (3.104 Å) strongly indicated a hydrogen bonding between H27 (and its symmetric H) and O2. $^1$H NMR at −50 °C reveals dramatically different chemical shifts for both imines (8.11 and 10.04 ppm), thus endorsing the hydrogen-bonding proposed. Yet, the dynamic imine coordination was indicated by the exchange peaks in ROESY-NMR and convergence of these imine peaks at higher temperatures as shown in VT-NMR data (Figure 3C). On the other hand, DOSY-NMR experiments suggested that the $\text{Bi}_2\text{O}_2$ ring of 6 was preserved in solution and no dissociation occurred. The structure of 6 suggests that similar species are formed when 1 is oxidized with $\text{N}_2\text{O}$ (Scheme 1).

At this point, we speculated that the dimeric nature of 6 could be the result of a rapid dimerization of a monomeric terminal Ar=Bi=O compound. Based on previous examples, we speculated that replacement of the imines with ketimines would favor the isolation of a monomeric species via tautomerization processes. To entertain this hypothesis, 5 was subjected to $\text{N}_2\text{O}$ in THF-$d_8$ (Figure 4A). Similar to 6, $^1$H NMR of the resulting orange-red solution indicated the formation of one single species. X-ray crystallography unequivocally determined that 7 was a monomeric organobismuth hydroxide (Figure 4B). The high quality of the crystals allowed the unambiguous assignment of the positions of the H1, H8a, H8b, and H10 (3 H). One of the Me groups in the ketimines converted into a CH$_2$, resulting in a reduction of the C–C length in C7–C8 [1.3552(16) Å], consistent with a double bond. The longer C7–N1 and Bi1–N2 distances [1.3832(15) and 2.6117(9) Å] compared to C9–N2 and Bi1–N1 [1.2848(14) and 2.2319(9) Å] also manifest the presence of an amido bond in one of the arms of the pincer. Interestingly, the OH points to a phenyl group of a m-Tp with a short H–phenyl centroid distance of 2.622 Å, indicative of a weak OH···π interaction. Due to the high tendency to form oxides or clusters through dehydration, reports on well-defined organobismuth hydroxides are limited; yet, 7 is noticeably stable.

The monomeric compound 7 represents a tautomeric form of a monomeric Ar=Bi=O, an elusive species which has yet to be reported. In the same way, 6 can be conceived as the result of a fast dimerization process of two molecules of monomeric Ar=Bi=O. The formation of hydroxide 7 highlights the high basicity of the O atom in Ar=Bi=O, which could be better described as a polarized Bi=O bond: Ar=Bi=O$^-$. Therefore, it is reasonable to assume that both 6 and 7 are fingerprints for the transient generation of such elusive species (int-I, both resonance structures depicted; Scheme 2), which rapidly dimerizes or tautomerizes to the more stable compounds 6 and 7.

**Scheme 2. Postulated Intermediates during Oxidation of Bi(I) with $\text{N}_2\text{O}$**

Having identified the intermediacy of Bi–O bonds after $\text{N}_2\text{O}$ activation, we explored the reduction of 6 and 7 to Bi(I) to sustain a putative catalytic cycle. Among other uses, HBpin has been utilized as a deoxygenation agent for amine and phosphine oxides as well as for the catalytic reduction of CO$_2$. Inspired by this reactivity, we treated 6 with 2.0 equiv of HBpin, which resulted in immediate formation of a dark purple solution (Scheme 3). Bismuthinidene 4 formed in 79% yield judging by $^1$H NMR. Similarly, the reduction of 7 gave 78% of 5. Meanwhile, ca. 1 equiv of HBpin was converted to a mixture of HO–Bpin (8) and (pin)B$_2$O (9).

At this point, we decided to merge this reactivity to unfold a catalytic system for the activation of $\text{N}_2\text{O}$ with Bi(I) compounds. Blank experiments demonstrated that no reaction occurs in the absence of Bi(I) (Table 1, entry 1). Catalytic $\text{N}_2\text{O}$ deoxygenation with HBpin proceeded smoothly at room temperature in the presence of 1 mol % of 4 or 5, with the TON reaching 54 and 89, respectively (entries 2 and 3). The higher efficiency of 5 over 4 could be ascribed to the higher stability of oxobismuth species 7 compared to 6. To our
Scheme 3. Reduction of 6 and 7 with HBpin

Table 1. Bi(I)-Catalyzed N₂O Deoxygenation with HBpin

| Entry | HBpin (x mol%) | time (h) | TON² | Table 2. N₂O Deoxygenation with HBpin

| Entry | Bi(0) (1 bar) | N₂O | THF-d₈, 25 °C | THF-d₈, 25 °C | THF-d₈, 25 °C | HGBpin | µmol, 1.0 equiv) in 1.25 mL of THF-d₈ at 25 °C.

| Entry | 8 | S/N ratio (%)² TON² |
|-------|---|---------------------|
| 1     | 4 (1.0) | 15 h | 0 | 97 | 36/31 | 6700 |
| 2     | 3 (1.0) | 15 h | 79 | 27/27 | 54 |
| 3     | 9 (1.0) | 15 h | 100 | 79/10 | 89 |
| 4     | 1 (1.0) | 15 h | 100 | 60/20 | 80 |
| 5     | 1 (0.5) | 15 h | 100 | 57/21 | 780 |
| 6     | 1 (0.5) | 15 h | 100 | 53/23 | 1520 |
| 7     | 1 (0.5) | 11 h | 90 | 36/31 | 6700 |

²Reaction conditions: 6 (17.8 µmol) or 7 (35.7 µmol), HBpin (71.4 µmol), mesitylene (35.7 µmol, 1.0 equiv) in 1.25 mL of THF-d₈ at 25 °C.

³Based on HBpin. Calculated by 1H NMR using mesitylene as internal standard. Determined by disappearance of the characteristic color of Bi(I).

In conclusion, this work demonstrates the capacity of bismuthinidines to catalytically activate N₂O in a Bi(I)⇄Bi(III) redox platform. The synthesis of sterically congested bismuthinidines using m-Tp substituents on the imines permitted isolation and characterization of catalytically relevant species such as bismuth oxide dimer 6 and bismuth hydroxide 7. Bis-imine and bis-ketimine N,C,N-chelated bismuthinidines provide the first main-group redox platform for catalytic N₂O decomposition. The ambient conditions and the very high catalytic efficiency make this system akin to transition-metal counterparts, unveiling an alternative opportunity for catalytic N₂O transformations.

REFERENCES

(1) (a) Prather, M. J. Time Scales in Atmospheric Chemistry: Coupled Perturbations to N₂O, NO, and O₃. Science 1998, 279, 1339−1341. (b) Hansen, J.; Sato, M. Greenhouse Gas Growth Rates. Proc. Natl. Acad. Sci. U. S. A. 2004, 101, 16109−16114. (c) Ravishankara, A. R.; Daniel, J. S.; Portmann, R. W. Nitrous Oxide (N₂O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century. Proc. Natl. Acad. Sci. U. S. A. 2004, 101, 16114. (d) Dameris, M. Depletion of the Ozone Layer in the 21st Century. Angew. Chem., Int. Ed. 2010, 49, 489−491.

(2) For examples of stoichiometric coordination, activation and functionalization of N₂O based on homogeneous and heterogeneous transition metal systems, see: (a) Leon’t’ev, A. V.; Fomicheva, O. A.; Proskurnina, M. V.; Zefirov, N. S. Modern Chemistry of Nitrous Oxide: The Dominant Ozone-Depleting Substance Emitted in the 21st Century. Science 2009, 326, 123−125. (c) Hansen, J.; Sato, M. Greenhouse Gas Growth Rates. Proc. Natl. Acad. Sci. U. S. A. 2004, 101, 16109−16114. (d) Dameris, M. Depletion of the Ozone Layer in the 21st Century. Angew. Chem., Int. Ed. 2010, 49, 489−491.
Oxide. Russ. Chem. Rev. 2001, 70, 91–104. (b) Parmon, V. N.; Panov, G. I.; Uriarte, A.; Noskov, A. S. Nitrous Oxide in Oxidation Chemistry and Catalysis: Application and Production. Catal. Today 2005, 100, 115–131. (c) Tolman, W. B. Binding and Activation of N₂O at Transition-Metal Centers: Recent Mechanistic Insights. Angew. Chem., Int. Ed. 2010, 49, 1018–1024. (d) Konsolakis, M. Recent Advances on Nitrous Oxide (N₂O) Decomposition over Non-Noble-Metal Oxide Catalysts: Catalytic Performance, Mechanistic Considerations, and Surface Chemistry Aspects. ACS Catal. 2015, 5, 6397–6421. (e) Severin, K. Synthetic Chemistry with Nitrous Oxide. Chem. Soc. Rev. 2015, 44, 6375–6386. and references therein.

(3) Lehner, N.; Dong, H. T.; Harland, J. B.; Hunt, A. P.; White, C. J. Reversing Nitrogen Fixation. Nat. Rev. Chem. 2018, 2, 278–289.

(4) (a) Yamada, T.; Hashimoto, K.; Kitaichi, Y.; Suzuki, K.; Ikeno, T. Nitrous Oxide Oxidation of Olefins Catalyzed by Ruthenium Porphyrin Complexes. Chem. Lett. 2001, 30, 268–269. (b) Zeng, R.; Feller, M.; Ben-David, Y.; Milstein, D. Hydrogenation and Hydrolylation of Nitrous Oxide Homogeneously Catalyzed by a Metal Complex. J. Am. Chem. Soc. 2017, 139, 5720–5723. (c) Zeng, R.; Feller, M.; Diskin-Posner, Y.; Shimom, L. J. W.; Ben-David, Y.; Milstein, D. CO Oxidation by N₂O Homogeneously Catalyzed by Ruthenium Hydride Pincer Complexes Indicating a New Mechanism. J. Am. Chem. Soc. 2018, 140, 7061–7064.

(5) Gianetti, T. L.; Annen, S. P.; Santiso-Quinones, G.; Reimer, M.; Dries, M.; Grützmacher, H. Nitrous Oxide as a Hydrogen Acceptor for the Dehydrogenative Coupling of Alcohol. Angew. Chem., Int. Ed. 2016, 55, 1854–1858.

(6) (a) Yamamoto, A.; Kitazume, S.; Pu, L. S.; Ikeda, S. Synthesis and Properties of Hydrodinitrodinitros(triphenylphosphine)cobalt(i) and the Related Phosphine-cobalt Complexes. J. Am. Chem. Soc. 1971, 93, 371–380. (b) Gianetti, T. L.; Rodriguez-Lugo, R. E.; Harmer, J. R.; Trinca, M.; Vogt, M.; Santiso-Quinones, G.; Grüntzmacher, H. Zero-Valent Amino-Olefín Cobalt Complexes as Catalysts for Oxygen Atom Transfer Reactions from Nitrous Oxide. Angew. Chem., Int. Ed. 2016, 55, 15323–15328. (c) Corona, T.; Company, A. Nitrous Oxide Activation by a Cobalt(ii) Complex for Aldehyde Oxidation under Mild Conditions. Dalton Trans. 2016, 45, 14530–14533.

(7) (a) Yamada, T.; Suzuki, K.; Hashimoto, K.; Ikeno, T. N₂O Oxidation of Phosphines Catalyzed by Low-Valent Nickel Complexes. Chem. Lett. 1999, 28, 1041–1044. (b) Yonke, B. L.; Reeds, J. P.; Zhao, P. Y.; Situ, L. R. Catalytic Dehydrogenation and Nondegenerate Oxygen Atom Transfer Employing N₂O and CO₂ as a M²⁺/M³⁺ Cycle Mediated by Group 6 M⁻¹ Terminal Oxico Complexes. Angew. Chem., Int. Ed. 2011, 50, 12342–12346. (c) Kiefer, G.; Jeanbourquin, L.; Severin, K. Oxidative Activation Reactions of Grignard Reagents with Nitrous Oxide. Angew. Chem., Int. Ed. 2013, 52, 6302–6305. (d) Saito, S.; Ohtake, H.; Umezawa, N.; Kobayashi, Y.; Kato, N.; Hirobe, M.; Higuchi, T. Nitrous Oxide Reduction-coupled Alkene-alkene Coupling Catalysed by Metalloporphyrins. Chem. Commun. 2013, 49, 8979–8981.

(8) (a) Power, P. P. Main-group Elements as Transition Metals. Nature 2010, 463, 171–177. (b) Martin, D.; Sorellhová, M.; Bertrand, G. Stable Singlet Carbene Mincs as Mimics for Transition Metal Centers. Chem. Sci. 2011, 2, 389–399. (c) Chu, T.; Nikonov, G. I. Oxidative Addition and Reductive Elimination at Main-Group Element Centers. Chem. Rev. 2018, 118, 3608–3680. (d) Weetman, C.; Inoue, S. The Road Travelled: After Main-Group Elements as Transition Metals. ChemCatChem 2018, 10, 4213–4228. (e) Melen, R. L. Frontiers in Molecular p-block Chemistry: From Structure to Reactivity. Science 2019, 363, 479–484.

(9) (a) Xiong, Y.; Yao, S.; Dries, M. Chemical Tricks To Stabilize Silanones and Their Heavier Homologues with E = O Bonds (E = Si–Ph): From Elusive Species to Isolable Building Blocks. Angew. Chem., Int. Ed. 2013, 52, 4302–4311. (b) Zhong, M.; Sinhababu, S.; Roeyck, H. W. The Unique β-Diketiminate Ligand in Aluminum(i) and Gallium(i) Chemistry. Dalton Trans. 2020, 49, 1351–1364. (c) Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. The Aluminy Anion: A New Generation of Alumini Molecules. Angew. Chem., Int. Ed. 2020, DOI: 10.1002/anie.202007530. (d) Loh, Y. K.; Aldridge, S. Acid-Base Free Main Group Carbyl Analouges. Angew. Chem., Int. Ed. 2020, DOI: 10.1002/anie.202008174.

(10) (a) Otten, E.; Neu, R. C.; Stephan, D. W. Complexation of Nitrous Oxide by Frustrated Lewis Pairs. J. Am. Chem. Soc. 2009, 131, 9918–9919. (b) Neu, R. C.; Otten, E.; Stephan, D. W. Bridging Modes of Phosphine-Stabilized Nitrous Oxide to Zn(C₆F₅)₂. Angew. Chem., Int. Ed. 2009, 48, 9709–9712. (c) Kelly, M. J.; Gilbert, J.; Tirföin, R.; Aldridge, S. Frustrated Lewis Pairs as Molecular Receptors: Colorimetric and Electrochemical Detection of Nitrous Oxide. Angew. Chem., Int. Ed. 2013, 52, 14094–14097. (d) Ménard, G.; Hatneau, J. A.; Cowley, H. J.; Lough, A. J.; Rawson, J. M.; Stephan, D. W. C-H Bond Activation by Radical Ion Pairs Derived from R,P(Al(C₆F₅))₂, Frustrated Lewis Pairs and N₂O. J. Am. Chem. Soc. 2013, 135, 6464–6469. (e) Mo, Z.; Kolychev, E. L.; Rit, A.; Campos, J.; Niu, H.; Aldridge, S. Facile Reversibility by Design: Tuning Small Molecule Capture and Activation by Single Component Frustrated Lewis Pairs. J. Am. Chem. Soc. 2015, 137, 12227–12230.
(15) Schwann, R. J.; Lein, M.; Coles, M. P.; Fitchett, C. M. Catalytic Oxidative Coupling Promoted by Bismuth TEMPOxide Complexes. *Chem. Commun.* 2018, 54, 916–919.

(16) Ramler, J.; Krummenacher, I.; Lichtenberg, C. Well-defined, Molecular Bismuth Compounds: Catalysts in Photochemically-induced Radical Dehydrocoupling Reactions. *Chem. Eur. J.* 2020, DOI: 10.1002/chem.202002219.

(17) Wang, F.; Planas, O.; Cornella, J. Bi(I)-Catalyzed Transfer-Hydrogenation with Ammonia-Borane. *J. Am. Chem. Soc.* 2019, 141, 4235–4240.

(18) (a) Planas, O.; Wang, F.; Leuttsch, M.; Cornella, J. Fluorination of Arylboronic Esters Enabled by Bismuth Redox Catalysis. *Science 2020*, 367, 313–317. (b) Planas, O.; Peciunikas, V.; Cornella, J. Bismuth-Catalyzed Oxidative Coupling of Arylboronic Acids with Triflate and Nonalflate Salts. *J. Am. Chem. Soc.* 2020, 142, 11382–11387.

(19) For an electrochemical H₂ generation catalyzed by Dostál's bismuthinidene, see: Xiao, W.-C.; Tao, Y.-W.; Luo, G.-G. Hydrogen Formation Using a Synthetic Heavier Main-group Bismuth-based Electro catalyst. *Int. J. Hydrogen Energy 2020*, 45, 8177–8185.

(20) (a) Simon, P.; de Proft, F.; Jambor, R.; Růžička, A.; Dostál, L. Monomeric Organoacontimony(I) and Organobismuth(I) Compounds Stabilized by an NCN Chelating Ligand: Syntheses and Structures. *Angew. Chem., Int. Ed.* 2010, 49, 5468–5471. (b) Vránová, I.; Alonso, M.; Lo, R.; Sedláč, R.; Jambor, R.; Růžička, A.; Proft, F. D.; Hofza, P.; Dostál, L. From Dibismuthenes to Three- and Two-Coordinated Bismuthinidenes by Fine Ligand Tuning: Evidence for Aromatic BiC₅N Rings through a Combined Experimental and Theoretical Study. *Chem. - Eur. J.* 2015, 21, 16917–16928.

(21) See Supporting Information for details.

(22) (a) Tokito, N.; Arai, Y.; Okazaki, R.; Nagase, S. Synthesis and Characterization of a Stable Dibismuthene: Evidence for a Bi-Bi Double Bond. *Science 1997*, 277, 78–80. (b) Sasamori, T.; Arai, Y.; Takeda, N.; Okazaki, R.; Furukawa, Y.; Kimura, M.; Nagase, S.; Tokito, N. Syntheses, Structures and Properties of Kinetically Stabilized Distibenes and Dibismuthes, Novel Doubly Bonded Systems between Heavier Group 15 Elements. *Bull. Chem. Soc. Jpn.* 2002, 75, 661–675.

(23) Strimb, G.; Föhnitz, A.; Raß, C. I.; Silvestru, C. A General Route to Monoorganopnicogen(III) (M = Sb, Bi) Compounds with a Pincer (N,C,N) Group and Oxo Ligands. *Dalton Trans. 2015*, 44, 9927–9943.

(24) (a) Breuning, H. J.; Königsmann, L.; Lork, E.; Nema, M.; Philipp, N.; Silvestru, C.; Soran, A.; Varga, R. A.; Wagner, R. Hydropalladium Organobismuth(III) Carbonate, Chalcogenides and Halides with the Pendant Arm Ligands 2-(MeNCH₂)C₆H₄ and 2,6-(Me₂NCH₂)C₆H₄. *Dalton Trans. 2008*, 1831–1842. (b) Chovancová, M.; Jambor, R.; Růžička, A.; Jirásko, R.; Čisarová, I.; Dostál, L. Synthesis, Structure, and Reactivity of Intramolecularly Coordinated Organoacontimony and Organobismuth Sulﬁdes. *Organometallics 2009*, 28, 1934–1941.

(25) (a) Hardman, N. J.; Twamley, B.; Power, P. P. (2,6-Mes₃H,C₅H,BiH₂, a Stable, Molecular Hydride of a Main Group Element of the Sixth Period, and Its Conversion to the Dibismuthene (2,6-Mes₃H,C₅H)₂BiH₂(2,6-Mes₃C₆H₄). *Angew. Chem., Int. Ed. 2000*, 39, 2771–2773.

(26) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. Homologous Series of Heavier Element Dipnicetenes 2,6-Ar₂H₃C₆E= and Its Conversion to the Dibismuthene (2,6-Mes₃C₆H,BiH₂, a Stable, Molecular Hydride of a Main Group Element of the Sixth Period, and Its Conversion to the Dibismuthene (2,6-Mes₃C₆H₄)₂BiH₂(2,6-Mes₃C₆H₄). *J. Am. Chem. Soc.* 1999, 121, 3357–3367.

(27) Breuning, H. J.; Haddad, N.; Lork, E.; Mehring, M.; Mügge, C.; Nolde, C.; Raß, C. I.; Schürmann, M. Novel Sterically Congested Monooorganobismuth(III) Compounds: Synthesis, Structure, and Bismuth-Arene π Interaction in ArBiXY (X = Y = Br, I; OH, 2,6-Mes₃C₆H₄). *Organometallics 2009*, 28, 1202–1211.

(28) Vránová, I.; Alonso, M.; Jambor, R.; Růžička, A.; Turek, J.; Dostál, L. Different Products of the Reduction of (N),C,N-Cleaved Antimony(III) Compounds: Competitive Formation of Monomeric Stibinidenes versus 1H-2,1-Benzazastiboles. *Chem. - Eur. J.* 2017, 23, 2340–2349.

(29) Organobismuth(III) Compounds. In *Organobismuth Chemistry*, 1st ed.; Suzuki, H.; Matano, Y., Eds.; Elsevier Science: Amsterdam, 2001; pp 21–245.

(30) (a) Matano, Y.; Nomura, H. Dimeric Triarylantimoniu Oxide: A Novel Efﬁcient Oxidant for the Conversion of Alcohols to Carboxyl Compounds. *J. Am. Chem. Soc.* 2001, 123, 6443–6444. (b) Matano, Y.; Nomura, H.; Hisanaga, T.; Nakano, H.; Shiro, M.; Imahori, H. Diverse Structures and Remarkable Oxidizing Ability of Triarylanthimoniu Oxides. Comparative Study on the Structure and Reactivity of a Series of Triarylpnicogen Oxides. *Organometallics 2004*, 23, 5471–5480.

(31) The denomination of syn- and anti- for explaining the orientation of arylbismuth oxo dimers is adopted from a previous report (ref 23) on these types of structures. A schematic explanation of this nomenclature is shown below.

(32) Wang, Y.; Hu, H.; Zhang, J.; Cui, Y.; Anionic and Lewis Acid Stabilized N-Heterocyclic Oxoboranes: Their Facile Synthesis from a Borinic Acid. *Angew. Chem., Int. Ed.* 2011, 50, 2816–2819.

(33) Smith, M. B.; March, J. March’s Advanced Organic Chemistry, 6th ed.; Wiley: Hoboken, NJ, 2007.

(34) (a) Pineda, L. W.; Janick, V.; Nembenna, S.; Roeksy, H. W. Synthesis and Structural Studies of Lead and Bismuth Organohalides. *Z. Anorg. Allg. Chem.* 2007, 633, 2205–2209. (b) Knispel, C.; Limberg, C. C-H Bond Activation in a Molybdenuroxo-Bismuth Compound. *Organometallics 2011*, 30, 3701–3703. (c) Vránová, I.; Jambor, R.; Růžička, A.; Hoffmann, A.; Herres-Pawlis, S.; Dostál, L. Antimony(III) and Bismuth(III) Amides Containing Pendant N-Donor Groups—a Combined Experimental and Theoretical Study. *Dalton Trans.* 2015, 44, 395–400. (d) Bresen, J.; Hinz, A.; Schulz, A.; Villinger, A. Trapping of Transient, Heavy Pnicogen-centred Biradicals. *Dalton Trans.* 2018, 47, 4433–4436.

(35) Battaglia, L. P.; Benamartini Corradi, A.; Pelizzi, C.; Pelosi, G.; Tarasconi, P. Chemical and Structural Investigations on Bismuth Complexes of 2,6-Di-acetylpyridine Bis(thiosemicarbazone). *Dalton Trans.* 2008, 47, 6590–6593. (c) Frichirová, A.; Svoboda, T.; Jambor, R.; Paděková, Z.; Růžička, A.; Erben, M.; Jirásko, R.; Dostál, L. Synthesis and Structural Study on Organoacontimony(III) and Organobismuth(III) Hydrides Containing an NCN Pincer Type Ligand. *Organometallics 2009*, 28, 5522–5528. (d) Roggan, S.; Limberg, C. Ziemer, B.; Siemons, M.; Simon, U. Reactivity and Properties of [−O-BiIII...O = Mo−]. *Inorg. Chem.* 2006, 45, 9020–9031.

(36) Ramachandran, P. V.; Chandra, J. S.; Ros, A.; Fernández, R.; Lassaletta, J. M.; Aggarwal, V. K.; Blair, D. J.; Myers, E. L.
Pinacolborane. In Encyclopedia of Reagents for Organic Synthesis; Wiley: 2017.

(37) (a) Köster, R.; Morita, Y. Oxidation of Organoboranes with Amine Oxides. Angew. Chem., Int. Ed. Engl. 1966, 5, 580−580.
(b) Hawkenwood, S.; Stephan, D. W. Syntheses and Reactions of the Bis-boryloxide O(Bpin)$_2$ (pin = O$_2$C$_2$Me$_4$). Dalton Trans. 2005, 2182−2187.

(38) (a) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. Borane-Mediated Carbon Dioxide Reduction at Ruthenium: Formation of C1 and C2 Compounds. Angew. Chem., Int. Ed. 2012, 51, 1671−1674.
(b) Bontemps, S.; Sabo-Etienne, S. Trapping Formaldehyde in the Homogeneous Catalytic Reduction of Carbon Dioxide. Angew. Chem., Int. Ed. 2013, 52, 10253−10255. (c) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. Ruthenium-Catalyzed Reduction of Carbon Dioxide to Formaldehyde. J. Am. Chem. Soc. 2014, 136, 4419−4425.
(d) Bagherzadeh, S.; Mankad, N. P. Catalyst Control of Selectivity in CO$_2$ Reduction Using a Tunable Heterobimetallic Effect. J. Am. Chem. Soc. 2015, 137, 10899−10901.
(39) HO-Bpin (8) reacted further with HBpin to yield (pinB)$_2$O (9). See ref 38d for an example of this reactivity.