

Communication

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Feng Wang, Oriol Planas, and Josep Cornella

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Bi(I)-Catalyzed Transfer-Hydrogenation with Ammonia-Borane

Feng Wang,[†] Oriol Planas[†] and Josep Cornella^{*}

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, Mülheim an der Ruhr, 45470, Germany.

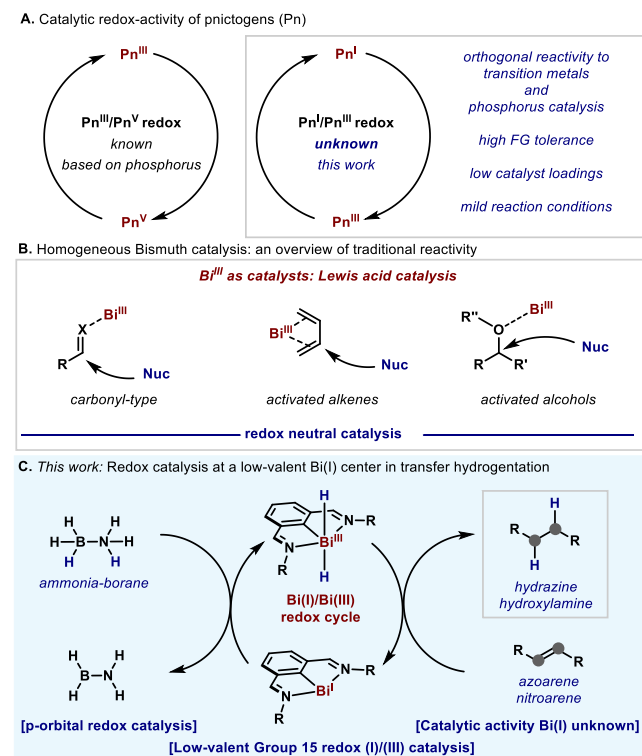
Supporting Information Placeholder

ABSTRACT: A catalytic transfer-hydrogenation utilizing a well-defined Bi(I) complex as catalyst and ammonia-borane as transfer agent has been developed. This transformation represents a unique example of low-valent pnictogen catalysis cycling between oxidation states I and III, and proved useful for the hydrogenation of azoarenes and the partial reduction of nitroarenes. Interestingly, the bismuthinidine catalyst performs well in presence of low-valent transition-metal sensitive functional groups and presents orthogonal reactivity compared to analogous phosphorus-based catalysis. Mechanistic investigations suggest the intermediacy of an elusive bismuthine species, which is proposed to be responsible for the hydrogenation and the formation of hydrogen.

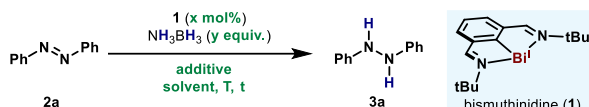
For over half a century, the use of noble metal catalysis has revolutionized the way chemists assemble molecules via the construction of new bonds.¹ The enormous impact of these metals at industrial level has led to their exploitation, becoming less abundant and hence more expensive. In recent years, an increasing attention has been placed in unlocking the potential of more abundant first-row transition metals thus becoming powerful sustainable alternatives.² In parallel, approaches that depart from transition metals have also gained momentum; for example the use of alkali and alkaline,³ main group,⁴ and the use of Frustrated Lewis Pairs,⁵ have become promising alternatives to transition metals (TM) thus emulating their behavior and reactivity. However, despite the wealth of literature in these areas, the quest for conferring TM-like *catalytic properties* to main group elements is still in its infancy.⁶ In this regard, the ability of pnictogens to maneuver between distinct oxidation states represents a promising approach. Recently, Radosevich reported a variety of P(III)/P(V) redox platforms, which show catalytic activity towards a variety of transformations (Figure 1A).⁷ This reactivity is based on highly strained P(III) compounds, where the lone pair becomes easily oxidizable and thus more prone to nucleophilic attacks and formal oxidative additions.⁸ Such groundbreaking approach opened the door to the possibility of performing catalytic redox processes beyond the TM block. With the aim of investigating unconventional catalytic redox processes of non-transition metals, we have recently started a program which focuses on the exploitation of the redox abilities of bismuth (Bi) to be applied in organic synthesis. Bi represents the last stable element in the periodic table,⁹ with properties at the interface of metalloids and main group.¹⁰ Importantly, Bi has been considered non-toxic and largely more abundant than commonly employed TM such as Pd, Rh or Ir,¹¹ thus highlighting its potential towards developing truly sustainable catalytic strategies. Yet, the use of bismuth in organic synthesis has been largely dominated by stoichiometric reactions based on Bi(V) or Bi(III) species, and catalytic strategies primarily focused on the soft Lewis-acid properties of Bi(III) salts (Figure 1B).¹² In addition, methods beyond the classic reactivity of Bi salts have recently attracted increasing attention.¹³ In contrast to the wealth of methods using high-valent Bi species,¹⁴ attention to its low-valent counterparts has been scarce. Low-valent Bi(I) compounds are known in the literature,¹⁵ yet seldom monomeric Bi species have been isolated.¹⁶ Generally, the formation of Bi(I) compounds is achieved through a highly unstable Bi(III) dihy-

dride, which rapidly extrudes H₂ upon ligand coupling.^{16,17} Inspired by these results, herein we present a transfer hydrogenation of azoarenes and nitro compounds with ammonia-borane (AB) catalyzed by a well-defined and stable Bi(I) complex. Preliminary mechanistic investigations point out at a catalytic platform involving extremely reactive Bi(III) hydride intermediates (Figure 1C).¹⁸ To the best of our knowledge, this is the *first example of a catalytic redox cycle in the pnictogens group maneuvering in a Pn(I)/Pn(III) redox cycle*.

Figure 1. (A) Catalytic redox-activity of pnictogens; (B) Typical reactivity of Bi(III) in catalysis; (C) Bi(I)/Bi(III) redox catalysis.



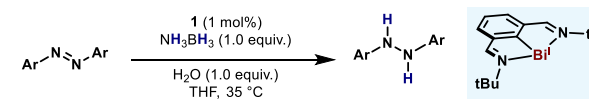
Initially, we attempted the transfer hydrogenation using a bismuthinidine complex (**1**)^{16b} as catalyst in THF at 50 °C (Table 1, entry 1). To our delight, **2a** was completely converted to **3a** using 1.0 equiv of AB as reducing agent. When the catalyst loading and the reaction time were reduced, lower yields were obtained (entry 2), but the addition of 2.0 equiv of AB using 1 mol% of **1** resulted in good yields of **3a** (entry 3). Yields were substantially diminished at lower temperatures (entry 4), but the reaction performed well in halogenated solvents (entry 5). Such reactivity is in stark contrast to the high reactivity of low-valent TM, which react with halogenated compounds leading to catalyst deactivation or decomposition. The use of other polar solvents (entries 6 and 7) was not beneficial, but noticeably, the addition of 1.0 equiv of H₂O improved the yield and reduced reaction times (entry 8). Furthermore, the reaction did not proceed in absence of catalyst (entry 9) or AB complex (entry 10).


Table 1. Optimization of the Bi(I)-catalyzed transfer hydrogenation.


entry	X	Y	solvent	T (°C)	t (h)	3a, yield (%) ^a
1	4	1	THF	50	24	99
2	1	1	THF	50	16	57
3	1	2	THF	50	16	86
4	1	2	THF	35	16	53
5	1	2	DCE	50	16	76
6	1	2	1,4-dioxane	50	16	87
7	1	2	acetone	50	16	45
8 ^b	I	I	THF	35	3	99 (99) ^c
9 ^b	-	1	THF	35	16	traces
10 ^b	1	-	THF	35	16	traces

^aYield calculated by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. ^bWith 1.0 equivalent of H₂O. ^cIsolated yield.

With these optimal reaction conditions in hand, we explored the influence of different substituents in the azoarene (**2**). As shown in Table 2, the protocol boded well with substrates bearing ester groups, without reduction of the carbonyl moiety (**3b**). Electron-rich azoarenes can also be reduced (**3c**), as well as substrates containing electron-withdrawing functionalities, such as fluoride (**3d**) and trifluoromethyl (**3e**). The presence of a bromide group at the *ortho* position of the reactive functionality did not inhibit the reactivity (**3f**). Azoarenes bearing substituents at the *meta* position also reacted smoothly under the optimized conditions (**3g**). Interestingly, unsymmetrical azoarenes in a push-pull electronic situation were also tolerated (**3h**). It is noteworthy that the presence of the iodide group did not affect the reaction outcome, further indicating the stability of **1** towards oxidative additions to labile bonds. Although cyclic compounds can also be completely reduced (**3i**), aromatic azoarenes has proven.¹⁹

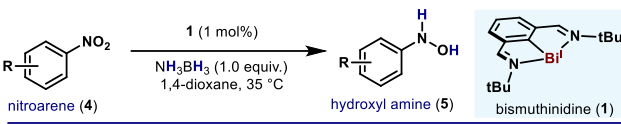
Table 2. Scope of the transfer hydrogenation of azoarenes.^a


3b , R =  , 99%	3c , R = Me, 97%	3d , R = F, 95%	3e , R = CF ₃ , 99%
3g , 98%	3h , 99% ^b	3f , 98%	3i , 99%

^aIsolated yields. ^bYield calculated by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard.

At this point, we decided to expand the protocol to other unsaturated functionalities such as nitroarenes (**4**, Table 3). Contrarily to the majority of TM-catalyzed reductions, this protocol is highly selective towards the formation of *N*-arylhydroxylamines.²⁰ With a slight modification from the optimized protocol,²¹ a variety of electronically distinct nitroarenes could be reduced in excellent yields. For example, simple nitrobenzene was reduced to *N*-phenylhydroxylamine (**5a**) in 89% yield. Electron-rich nitroarenes are also amenable to this reactivity (**5b**), as well as substrates containing carbon-halogen bonds such as bromide (**5c**) and iodide (**5d**). Compounds bearing unsaturated functionalities such as alkyne (**5e**), nitrile (**5f**) and alkene (**5g**) were also obtained in excellent yields. Interestingly, when 2-phenylnitrobenzene (**4h**)

was subjected to the reaction conditions, excellent yields were obtained of the corresponding *N*-hydroxylamine (**5h**). This result is complementary to P(III) catalysis, with which intramolecular Cadogan-type reactions *en route* to carbazole have been observed.⁷¹ Finally, sterically congested nitroarenes delivered the corresponding *N*-hydroxylamines (**5i**) albeit in lower yields.

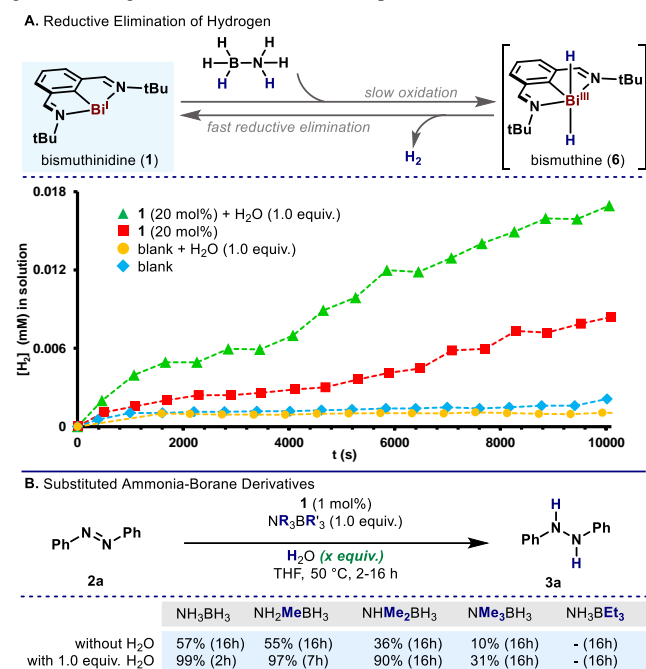
Table 3. Scope of the transfer hydrogenation of nitroarenes.^a


5a , 89%	5b , R = Me, 94%	5c , R = Br, 85%	5d , R = I, 88%
5f , 91%	5g , 82%	5h , 75%	5e , 67%
			5i , 22%

^aIsolated yields.

The unprecedented catalytic activity of such Bi(I) complexes led us to explore the operative mechanism governing this homogeneous transformation (Scheme 1).²² Firstly, the ability of **1** for catalytic dehydrogenation of AB was tested. Thus, 1.0 equiv of AB was mixed with 0.2 equiv of Bi(I) complex in THF-*d*₈ and the formation of H₂ in solution was monitored (Scheme 1A, red). In absence of Bi(I) complex, no H₂ was observed after 150 min,²³ indicating that Bi(I) promotes a slow dehydrogenation of AB (Scheme 1A, blue and yellow). Furthermore, during our optimization studies we noticed a dramatic change in rate when water was added (Table 1, entry 8). With this result in mind, we tested the effect of H₂O in the dehydrogenation of AB catalyzed by Bi(I). Indeed, the addition of 1.0 equiv of H₂O caused an increase in rate for the formation of H₂ (Scheme 1A, green). Based on Dostál observations,¹⁶ we speculated that the formation of H₂ is derived from a highly unstable bismuthine (**6**).²⁴ The positive effect of H₂O is proposed to arise from H-bonding from AB and water, thus facilitating a plausible oxidation of **1** to **6**, which upon rapid H₂ extrusion regenerates species **1**. Indeed, to further evaluate the effect of H₂O in the reaction, a series of experiments with alkylated derivatives of AB were carried out (Scheme 1B). When the reaction was performed with NMe₃BH₃ as reducing agent, only a 10% of **3a** was obtained after 16 h. Moreover, when NH₂MeBH₃ and NHMe₂BH₃ complexes were employed, a 55% and 36% of **3a** was obtained, respectively. These results clearly indicate protons of AB play a key role in the transfer hydrogenation. Subsequently, the same reactions were performed in presence of 1.0 equiv of H₂O. Interestingly, with NMe₃BH₃ 31% of **3a** was observed, improving the yield of the anhydrous reaction. With NHMe₂BH₃ and 1.0 equiv H₂O the yield was improved to 90% after 16 h, and with NH₂MeBH₃ complex the reaction time was dramatically reduced to fully convert **2a** to **3a**. These results support the experimental observations in Scheme 1A. As control, the reaction in presence of NH₃BEt₃ did not lead to conversion of the starting material even after 16 h, which indicates the relevance of the hydride source of AB.

Scheme 1. (A) Dehydrogenation of AB with Bi(I) and (B) transfer hydrogenation using different amine borane complexes.

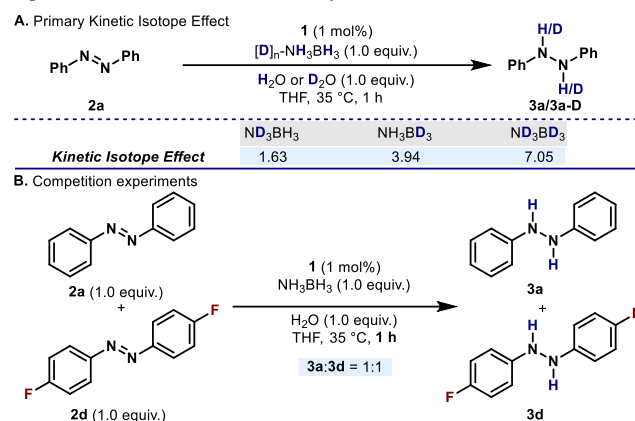


To further evaluate the formal oxidation *en route* to bismuthine **6**, primary kinetic isotope effects were measured using deuterium labeled AB (Scheme 2A). When the reaction was performed with 1.0 equiv ND₃BH₃ and 1.0 equiv of D₂O (rapid D-exchange between H₂O and ND₃BH₃ would result in misleading KIE values) a primary KIE value of 1.63 was obtained. With 1.0 equiv of labeled NH₃BD₃, a higher KIE value of 3.94 is observed. Finally, when the reaction was performed with 1.0 equiv ND₃BD₃, a large KIE value of 7.05 was obtained. These results suggest a mechanistic scenario in which both N–H and B–H bonds are broken in the rate-determining step (RDS).²⁵ Furthermore, a competition experiment between two electronically distinct azoarenes was performed (Scheme 2B). When 1.0 equiv of **2a** and 1.0 equiv of **2d** were mixed with 1.0 equiv of AB in the presence of 1 mol% of **1**, a 1:1 mixture of **3a** and **3d** was obtained after 1 h, suggesting that azoarenes are not participating in the RDS of this transformation.²⁶ These experiments point out to an scenario in which Bi(I) and AB are both involved in the RDS. However, the rate acceleration observed when H₂O is present in the system suggests that H₂O might interact with AB through H-bonding, and also participate in the RDS.²⁷

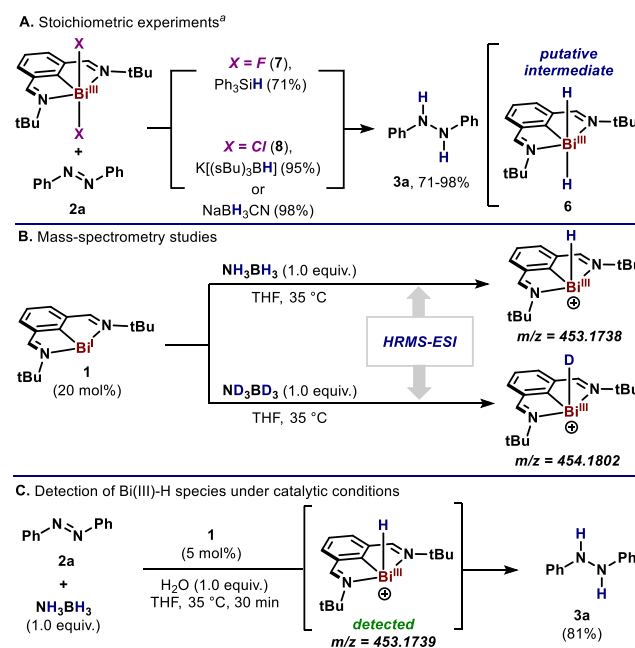
Bi(III)–H compounds are known to be highly unstable and reactive, which complicates their characterization as potential intermediates.^{16a} However, a series of experiments were designed to elucidate the presence of such elusive species (Scheme 3). Hence, when the reaction was performed with fluorobismuthine **7** and Ph₃SiH, **3a** was obtained in 71% yield. Equally, when **8** was mixed with 2.0 equiv K-Selectride or NaBH₃CN, **3a** was obtained in 95% and 98% yield respectively, together with Bi(I),¹⁹ indicating that both H in **3a** derive from the hydridic sources. Importantly, all these reactions afforded Bi(I) (**1**) and H₂ when no azobenzene was present in the mixture.¹⁶ While efforts to detect these intermediates by NMR spectroscopy were unsuccessful, we decided to investigate the dehydrogenation of AB by HRMS techniques. Indeed, when **1** is mixed with 5.0 equiv. of AB, a peak corresponding to [6–H]⁺ (C₁₆H₂₄BiN₂⁺, experimental: *m/z* = 453.1738; simulated: *m/z* = 453.1737) was observed (Scheme 3B), thus suggesting the formation of Bi(III)-hydride species.²⁸ Similarly, when AB was replaced by its deuterated analog, a mass for the Bi(III) deuteride was detected (C₁₆H₂₃DBiN₂⁺, experi-

mental: *m/z* = 454.1802; simulated: *m/z* = 454.1801). Additionally, the same Bi(III) hydride species was detected when the transfer hydrogenation of **2a** was performed under catalytic conditions and analyzed by HRMS (Scheme 3C). Taken together, these results indicate formation of Bi(III) hydrides in the dehydrogenation of AB,¹⁶ which further react in presence of azoarene **2a** to obtain **3a**. Although different scenarios could be foreseen from such hydridic intermediate, further computational and spectroscopic evidence is needed to fully understand its role in the formation of **3a**. Indeed, these studies are now being pursued in our laboratory.

Scheme 2. (A) Kinetic Isotope Effect experiments. (B) Competition experiment between two electronically different azoarenes.



Scheme 3. (A) Stoichiometric and (B and C) Mass Spectrometry studies.



^a 2.0 equivalents of reducing agent.

In conclusion, this work demonstrates the capacity of bismuth compounds to be engaged in *catalytic redox transformations*. The described protocol, which is a unique example of Bi(I) catalysis, resulted useful for the transfer hydrogenation of azoarenes and nitroarenes with AB as hydrogen surrogate. Preliminary mechanistic investigations suggest the intermediacy of highly reactive and elusive Bi(III) hydrides. These results constitute a unique proof-of-concept of a pnicogen operating between oxidation states I and III to mimic transformations typically performed by TM-catalysts.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and analytical data (^1H and ^{13}C NMR, HRMS) for all new compounds. This material is available free of charge via the internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

E-mail: cornella@kofo.mpg.de

Notes

†F.W. and O.P. contributed equally.

The authors declare no competing financial interest.

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(26) No reaction between **1** and **2a** or H₂O was observed neither in catalytic nor stoichiometric conditions. See Supporting Information for details.

(27) Although **1** can dehydrogenate AB in the absence of H₂O, the presence of 1.0 equiv. of H₂O accelerates the dehydrogenation step (Scheme 1A). In these cases, interaction of H₂O and AB through H-bonding networks is postulated, which results in an effect of H₂O in the rate-determining step. For references, see: (a) Dihydrogen vs Hydrogen Bonding in the Solvation of Ammonia Borane by Tetrahydrofuran and Liquid Ammonia, Ingram, D. J.; Headen, T. F.; Skipper, N. T.; Callear, S. K.; Billing, M.; Sella, A. *Phys. Chem. Chem. Phys.* **2018**, *20*, 12200; (b) Belkova, N. V.; Epstein, L. M.; Filipov, O. A.; Shubina, E. S. Hydrogen and Dihydrogen Bonds in the Reactions of Metal Hydrides. *Chem. Rev.* **2016**, *116*, 8545; (c) Stephens, F. H.; Pons, V.; Baker, T. Ammonia-Borane: the Hydrogen source *par excellence*? *Dalton Trans.* **2007**, 2613

(28) The same *m/z* is observed when the reaction of **8** with NaBH₃CN is analyzed by HRMS after 4 h reaction time. This result further supports the notion that Bi(III)-H are indeed involved in the transfer hydrogenation.

