Bismuth Redox Catalysis: An Emerging Main-Group Platform for Organic Synthesis

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ABSTRACT: Bismuth has recently been shown to be able to maneuver between different oxidation states, enabling access to unique redox cycles that can be harnessed in the context of organic synthesis. Indeed, various catalytic Bi redox platforms have been discovered and revealed emerging opportunities in the field of main group redox catalysis. The goal of this perspective is to provide an overview of the synthetic methodologies that have been developed to date, which capitalize on the Bi redox cycling. Recent catalytic methods via low-valent Bi(II)/Bi(III), Bi(I)/Bi(III), and high-valent Bi(III)/Bi(V) redox couples are covered as well as their underlying mechanisms and key intermediates. In addition, we illustrate different design strategies stabilizing low-valent and high-valent bismuth species, and highlight the characteristic reactivity of bismuth complexes, compared to the lighter p-block and d-block elements. Although it is not redox catalysis in nature, we also discuss a recent example of non-Lewis acid, redox-neutral Bi(III) catalysis proceeding through catalytic organometallic steps. We close by discussing opportunities and future directions in this emerging field of catalysis. We hope that this Perspective will provide synthetic chemists with guiding principles for the future development of catalytic transformations employing bismuth.

KEYWORDS: Main group catalysis, redox cycling, organobismuth, organic synthesis, heavy elements

1. INTRODUCTION

Catalysis based on transition metals (TMs) has undoubtedly had a profound impact in synthetic chemistry, ranging from laboratory routes to industrial-scale processes. One of the key underlying principles for the success of TM catalysis lies on their facile redox cycling between different oxidation states, which is coupled with bond formation or cleavage in its coordination sphere. For decades, such redox properties were believed to be the realm of TMs, and elements beyond the d-block were certainly not considered for such purposes. However, such dogmatic belief has been recently challenged, as many main group elements have been demonstrated to undergo elementary redox reactions that were once believed to be reserved for TMs. It is now common to see a growing number of articles in which s- and p-block elements undergo oxidative addition, reductive elimination, etc., leading to reactivity that resembles that of TMs and, in some instances, complements them. Despite the wealth of literature on the development of stoichiometric redox reactivity by main group elements, the development of efficient catalytic redox processes is challenging and is still in its infancy.

A major challenge is that unlocking catalytic redox cycle in main group elements requires a complete redesign of the approach when compared to TMs, because of the different electronic situation encountered for such elements (Figure 1).

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elements generally occur unidirectionally in a stoichiometric fashion, facilitated by strong thermodynamic driving forces. Hence, the p-block products in the redox reactions are often thermodynamic sinks, and their recycling toward catalytic protocols becomes problematic. For example, oxidative addition of E–H or C–X (E = H, C, N, O; X = F, Cl, Br, I) bonds to low-valent group 13 or 14 compounds is often favorable, but reductive elimination from the high-valent compounds of these elements is challenging. In contrast, C–H, C–C, or C–X (X = F, Cl) bond formation via reductive elimination from high-valent group 16 or 17 compounds is well-established, yet, oxidative addition to low-valent compounds of these elements is rare. Because of such biased thermodynamics between low-valent and high-valent species, merging redox elementary steps into redox cycling remains a tremendous challenge for the aforementioned p-block elements.

The group 15 elements, or pnictogens, are located in a transitional position on the p-block from a reactivity standpoint. Hence, a bidirectional Pn(n)/Pn(n+2) redox couple at group 15 elements should be viable. Considering the foregoing pnictogen properties, the Radosevich group pioneered phosphorus redox catalysis via a P(III)/P(V) oxidation of organophosphorus compounds also found synthetic applications as transition-metal ligands in several stoichiometric oxidative ligand coupling events. 

Traditionally, the catalytic utility of Bi(III) compounds in synthesis was limited to nonredox soft Lewis acid catalysis such as carbonyl and diene activation. Organobismuth(III) compounds also found synthetic applications as transmetalation reagents, because of the lability of Bi(III)–C bonds. In the presence of strong oxidants, these compounds undergo oxidation leading to organobismuth(V) compounds, which have been applied as oxidants in synthesis. Moreover, the labile nature of the Bi(V)–C bond has also been employed in several stoichiometric oxidative ligand coupling events toward C–C or C–X bond formation. In heterogeneous electrocatalysis or photocatalysis, Bi is frequently encountered as a dopant in materials in order to advance performance (e.g., selectivity and efficiency) in CO2 reduction, water splitting, and dinitrogen reduction. Despite these seminal reports indicating the rich redox chemistry of bismuth, the development of catalytic redox processes for organic synthesis have been largely overlooked. In this Perspective, we describe how the area of bismuth redox catalysis has flourished with illustration of recent developments in Bi(II)/Bi(III), Bi(I)/Bi(III), and Bi(III)/Bi(V) redox cycles. We aim to show design principles for different redox cycles toward new catalytic transformations. Albeit not via redox cycling, we also provide an example of redox-neutral Bi(III) catalysis via elementary organometallic steps. We believe that this Perspective provides a summary of the unique reactivity that makes bismuth a versatile element for redox catalysis, with properties that go beyond a mere TM alternative.

2. LOW-VALENT CATALYSIS

Unlike the lighter pnictogen elements, Bi has been shown to expand beyond the canonical Pn(III)/Pn(V) redox pair (see Section 3), enabling redox cycling at a rather unique low-valent platform, and hence, explore its reductive properties. In this section, we describe Bi(II)/Bi(III) and Bi(I)/Bi(III) redox cycles and the organic transformations derived thereof.

2.1. Low-Valent Bi(II)/Bi(III) Catalysis. The current examples of other group 15 elements in redox catalysis capitalize on the two-electron Pn(n)/Pn(n+2) redox pair for productive catalysis. In contrast, bismuth offers a unique opportunity for reactivity beyond such canonical redox pair through one-electron Bi(II)/Bi(III) redox processes.

As a seminal example of Bi(II) radical intermediates for synthetic use, Yamago reported organobismuthine-mediated radical polymerization reactions in 2007 (Figure 2). It was proposed that a bismuthine promoter undergoes Bi–C bond homolysis to generate alkyl radical 2 and Bi(II) radical 3 through thermal decomposition or radical initiation by a substochiometric amount of 2,2′-azobis(isobutyronitrile) (AIBN). The resulting Bi(II) species 3 promotes radical polymerization via the intermediacy of alkylbismuthine 4 that can further promote polymerization through homolytic Bi–C cleavage, enabling highly controlled living radical polymerization.

While transient Bi(II) species have been proposed in polymerization reactions, in 2014, Iwamoto first reported a persistent Bi(II) radical that is in equilibrium with its dimer in solution. Later, Coles reported the first monomeric Bi(II) species that is stable both in solution and in the solid state (Figure 3). Building on this seminal work on the isolable
Bi(II) species, in 2018, Coles reported a Bi(II)/Bi(III) redox cycle in a catalytic dehydrocoupling reaction of TEMPO radical (11) and phenylsilane using Bi(II) complex 7 as a catalyst.37 This stable and isolable complex (7) supported by bis(amide)disiloxane ligand was previously shown to exhibit one-electron reducing character in a stoichiometric manner.38 Merging its reducing character and the reactive nature of Bi(III)−O bonds,39 the catalytic dehydrocoupling of TEMPO (11) and phenylsilane was achieved, albeit under high temperatures and long reaction times. In this reaction, 7 undergoes radical recombination with TEMPO (11) to generate Bi(III)−TEMPOxide intermediate 9. This resulting Bi(III) species is then proposed to undergo metathesis with the Si−H bond in phenylsilane to produce the dehydrocoupling product 12 and a Bi(III)−hydride species 10. The putative Bi(III)−hydride species 10 was previously shown to oxidatively generate H2.38 Which would regenerate the Bi(II) catalyst 7 and close the Bi(II)/Bi(III) redox cycle.

An analogous Bi(II)/Bi(III) cycle was demonstrated by Lichtenberg using a diaryl(bismuth)thiolate precatalyst 8.40 It is proposed to generate a transient Bi(II) species upon UV irradiation via Bi−S bond homolysis and initiate the aforementioned Bi(II)/Bi(III) cycle toward dehydrocoupling. The comparatively faster reaction rates were achieved by in situ generation of the presumed catalytically active Bi(II) species.

In 2019, Lichtenberg also demonstrated a radical cycloisomerization of δ-iodo-olefins using a TM bismuthane catalyst.

2.2. Low-Valent Bi(I)/Bi(III) Catalysis. While the 6σ nonbonding lone pair in Bi(III) compounds is relatively low in energy and rather inert,45 the 6p lone pair lone pair in Bi(I) complexes has been shown to be nucleophilic and readily oxidized. Since the seminal report by Tokitoh in 1997, organobismuth(III) compounds have largely been reported as oligomeric or dimeric structures.43 It was not until 2010, when Dosta reported the first monomeric, well-defined organobismuth(I) complex supported by an N,C,N-pincer ligand (Figure 5).44 Access to this isolable bismuthinidene is feasible due to its stability rendered by the two N atoms in the imine arms, which coordinate to the low-lying Bi empty p-orbital.

In addition, the 6p lone pair in the pz orbital perpendicular to the ligand plane, is stabilized further through delocalization across the p–p bond of the ligand.

Building upon Dosta’s complex (23), in 2019, our group demonstrated that an analogous Bi(I) complex 24 is a competent catalyst in the context of transfer hydrogenation (Figure 6).45 Under the optimized reaction conditions, the complex 24 catalyzes the transfer hydrogenation from ammonia borane to either azoarenes or nitroarenes across the N−N or N−O π-bond, respectively, with good functional group tolerance. Azoarenes containing electron-donating or withdrawing groups can be reduced to the corresponding hydrazines in good yields (26–28), and an unsymmetrical azoarene in a push–pull situation was also well-tolerated (29). A bromide substituent on the ortho-position did not affect the

Figure 3. Bismuth-catalyzed dehydrocoupling of TEMPO and hydrosilanes via a Bi(II)/Bi(III) redox cycle.

Figure 4. Cycloisomerization of δ-ido-olefins using a TM bismuthane catalyst.

Figure 5. First stable monomeric N,C,N-chelated bismuthinidene and the Bi valence orbitals.
reactivity (30). Analogously, nitroarenes were reduced into the corresponding N-hydroxylamines in good yields, which complements TM-catalyzed reduction reactions.46 Electron-donating group (31), halide substituents (32, 33), and unsaturated functionality (34) were well-tolerated. 2-Phenyl-nitrobenzene was selectively reduced to the N-hydroxylamine 35 without formation of carbazole, which is complementary to the Cadogan-type P(III) catalysis. 47 In analogy with the intermediacy of the P(V)-dihydride in the previously described transfer hydrogenation via a P(III)/P(V) cycle, it is proposed that this catalytic cycle also involves the intermediacy of organobismuth(III) hydrides, such as 25, that can be detected by HRMS in the reaction mixture.17a However, the detailed mechanism including Bi−H bond formation/cleavage and N−H bond formation in the products is yet unknown.

Another example of the low-valent Bi(I)/Bi(III) redox platform can be found in the catalytic activation of nitrous oxide (N₂O) (Figure 7A).48 Exposure of the Bi catalyst 24, used in the transfer hydrogenation, to N₂O atmosphere (1 bar) resulted in the rapid liberation of N₂ and the formation of a putative dimeric bismuth oxide species. The resulting oxo species can be detected by HRMS—also observed in related bismuth oxo or sulfido dimer precedents49—but it could not be isolated or crystallographically characterized because of its thermal instability. In an attempt to characterize the organobismuth(III) intermediates, two new Bi(I) complexes were synthesized which were supported by aldimines (36) and ketimines (37) bearing m-terphenyl substituents. 50 Upon exposure to N₂O, the complex 36 afforded a dimeric bismuth oxide 38 with a [Bi₂O₂] core as its anti-isomer which was identified by single-crystal X-ray crystallography (Figure 7B). By contrast, the ketimine-supported 37 gave a monomeric bismuth hydroxide (40), presumably as a result of deprotonation of one of the Me groups in the backbone. These observations suggest the involvement of a transient monomeric bismuth oxide (39) upon O-atom abstraction from N₂O, which subsequently undergoes dimerization or deprotonation via the highly polarized Bi=O bond. Eventually, treating complexes 38 and 40 with pinacolborane (HBpin, 2 equiv) resulted in regeneration of 36 and 37, respectively, and formation of the mixture of HOBpin (41) and O(Bpin)₂ (42).

With validated oxidation and reduction as potential catalytic elementary steps, catalytic reactions were performed using these Bi(I) catalysts 36, 37, and 24. Indeed, the catalysts drive N₂O deoxygenation with TON of 54, 89, and 80, respectively. The most reactive 24 toward N₂O enabled lowering the catalyst loading to 0.01 mol % and enhancing the TON to 6700 (TOF ≈ 52 min⁻¹). This is an unprecedented catalytic activation of N₂O by main group elements, 51−53 which performs comparable or beyond TM deoxygenation catalysis.54−57 Albeit restricted to HBpin, this work reveals the potential of Bi catalysts for O-atom transfer (OAT), which can eventually be applied to organic substrates in catalytic oxidative transformations.

The catalytic utility of the N,C,N-chelated bismuthinidenes via a Bi(I)/Bi(III) redox cycle has been further expanded for hydrodefluorination (HDF) (Figure 8A).58 In this case, new bismuthinidenes 43 and 44 are employed, featuring oxazolines as pendant supporting arms, which is distinct from the previously reported Bi(I) complexes (i.e., 24, 36, 37). While HDF of hexafluorobenzene using the catalyst 24 (5 mol %) gave a trace amount of the product (53) in the presence of diethylsilane (2.4 equiv), the use of the newly designed catalysts 43 and 44 supported by a 2,6-bis(oxazolyl)phenyl...
Figure 8. (A) Bismuth-catalyzed hydrodefluorination (HDF) of polyfluorobenzene with diethylsilane. (B) Proposed mechanism of HDF. (C) Validation of C−F oxidative addition and C−H reductive elimination at the Bi center.

(Phbox) scaffold resulted in improvement to 40% and 74% yields, respectively. The structure of 43 and 44 that contains elongated Bi−C bonds and longer Bi−N bonds indicates that the advanced reactivity is achieved by virtue of more localized 6p lone pair orbital in 43 and 44 compared to that in complex 24 (Bi−C: 2.193(6) Å for 43, 2.201(4) Å for 44, 2.146(18) Å for 24; Bi−N: 2.502(3) and 2.525(3) Å for 43, 2.5142(18) and 2.5359(19) Å for 44, 2.492(8) and 2.502(9) Å for 24). This method hydrodefluorinates a variety of polyfluorobenzenes under mild conditions. Pentfluoropyridine and pentfluorobenzene with a strong electron-withdrawing group underwent HDF to give the products (49, 50) in quantitative yields at ambient temperature using 43. Bi-HDF (43) and HDF (44) of highly fluorinated phosphine are viable at 60 °C. Partially fluorinated substrates can be defluorinated (54−56), using 44 as a catalyst in moderate yields. No directing effect was observed (55), providing orthogonal selectivity to TM catalysis.59 Polyfluorobenzenes bearing an electron-donating group were found to be challenging, as similarly observed in HDFs using TM catalysts.50 Mechanistically, it is proposed that the Bi(I) catalyst 43 undergoes intermolecular oxidative addition (OA) of C(sp2)−F bond to give fluoroarylbiisuthine 45 (Figure 8B). Subsequent ligand metathesis (LM) with diethyilsilane (57) leads to the formation of hydroxyarylbiisuthine 47. It was found that a substoichiometric amount of 57 can be used as a 2 equiv hydride source, giving diethyl-silorosilane (58) upon completion of the reactions. Lastly, reductive elimination (RE) of C−H bond gives the HDF product 49 and regenerates the Bi(I) catalyst 43 to close the catalytic redox loop.

Each elementary step of the cycle was studied and validated experimentally (Figure 8C). In the stoichiometric reaction with pentafluoropyridine (48), it was shown that Bi(I) complex 43 undergoes C−F OA to give a fluoroarylbiisuthine 45 (Figure 8C, path a). It was observed that bismuthine 45 interconverts with other Bi species in the reaction mixture, but it could be characterized by multinuclear one-dimensional (1D) and two-dimensional (2D) nuclear magnetic resonance (NMR) spectroscopy. Subsequent addition of diethyilsilane to this mixture resulted in the formation of HDF product 49 and regeneration of Bi(I) complex 43. It was hypothesized that the labile Bi−F bond in 45 is attributed to the observed interconversion, and the isolation of cationic Bi(III) species 46 was attempted using LiOTf (Figure 8C, path b). Indeed, a stable cationic Bi(III) complex 46 was obtained, which was characterized by single-crystal X-ray crystallography. Upon treating 46 with LiAlH4 (0.5 equiv), the formation of hydroxyarylbiisuthine 47 was observed, which at elevated temperature, gave HDF product 49 and the Bi(I) complex 43. These three elementary steps, OA, LM, and RE, are akin to those in a well-defined P(III)/P(V) synthetic cycle for HDF previously demonstrated by Radosevick.51 While a catalytic OA/LM/RE cycle in a Pn(III)/P(V) manifold is considered yet challenging, the Bi(I)/Bi(III) redox cycle has enabled a catalytic cycle of such sequence by a main group complex, which is conventionally confined to TM catalysis. It is also shown that this N,C,N-chelated Bi platform for a Bi(I)/Bi(III) redox cycle is sufficiently robust to be applied in an electrocatalytic hydrogen evolution reaction (HER). The bismuthinidene 24 was in situ generated from the parent Bi(III) by electrochemical reduction, which oxidatively evolves hydrogen in the presence of acetic acid.62

3. HIGH-VALENT Bi(III)/Bi(V) CATALYSIS

Seminal work that capitalize upon the redox properties of organobismuth(III) in catalysis was reported by Barton and Motherwell in 1981, in which a Ph3Bi catalyst (59) was engaged with N-bromosuccinimide (NBS) as a stoichiometric oxidant for the C−C scission in 1,2-diols (Figure 9). Similar
to the previously reported oxidative reactions by Bi(V) reagents, the stochiometric oxidation of an α-glycol 61 by triphenylbismuth carbonate resulted in the formation of benzaldehyde 62 presumably via a Bi(V) intermediate 60. In this reaction, Ph₃Bi was formed in quantitative yield 69, and thus, the catalytic reactions were readily achieved by slow addition of NBS for regeneration of Bi(V) species. Related oxidative reactivity has also been reported using Ph₅Sb. However, in these examples, the organometallic compounds are mere oxidants and the Bi–C bonds remain intact throughout the catalysis.

Stoichiometric examples where the aryl ligands on organobismuth(V) complexes are engaged in reactivity can be found in the arylation of organic compounds through oxidative ligand coupling or formal reductive elimination. In order to advance these stoichiometric reactions to catalysis, the oxidation step (Bi(III) → Bi(V)) should be compatible with other elementary steps, and after ligand coupling, the commonly reactive aryl group must be reincorporated. In 2020, a demonstration of bismuth redox catalysis via canonical organometallic elementary steps in a Bi(III)/Bi(V) platform was described in the catalytic fluorination of aryl boronic esters (Figure 10A).55 A bismuth catalyst 63 supported by a diaminonic bis-aryl sulfoximine ligand is used to enable Bi(III)/Bi(V) redox cycling, where the NCF₃ coordinates to the Bi center as a weak ligand. With this ligand platform, Bi(III) catalyst 63 (10 mol %) drives fluorination of aryl boronic esters in the presence of 2,6-dichloro-1-fluoropyridinium tetrafluoroborate (67, 1 equiv) and sodium fluoride (5 equiv). Boronic esters with para-substitution are generally well-tolerated 70, 71. Those with meta- or ortho-substitution are amenable but relatively more challenging 72–75. Notably, the reaction did not proceed in the absence of the bismuth catalyst 66.

The catalytic Bi(III)/Bi(V) redox cycle is proposed for this fluorination on the basis of stoichiometric reactivity and identification of key intermediates (Figure 10B). It is proposed that the Bi(III) catalyst 63 first undergoes transmetalation with an aryl boronic ester to generate phenylbismuthine 65. The complex 65 is then oxidized by fluoropyridinium reagent 67 to afford a high-valent Bi(V) species 66 that is stabilized by coordination of the pendant NCF₃ moiety. The resulting Bi(V) species 66 undergoes reductive elimination of fluoroarene 69 to regenerate Bi(III) species 64, enabling Bi(III)/Bi(V) redox cycling. These elementary steps, including transmetalation, oxidative addition, and reductive elimination, have all been confirmed to proceed stoichiometrically (Figure 10C). The transmetalation product 65 was crystallographically characterized, and the following oxidation step yielded the fluorination product 69 and regenerated the Bi(III) catalyst 63. The Bi(V) intermediate 66 was independently synthesized and shown to undergo reductive elimination of C–F bond to give 69. Indeed, they are reminiscent of those in classic TM-catalyzed cross-coupling reactions. However, this Bi(III)/Bi(V) redox catalysis does not merely mimic TM catalysis but enables a catalytic reaction that is considered to be challenging with TMs.57–70 This chemistry exhibits the potential of bismuth redox catalysis to unveil new reactions unique to bismuth.

In addition, it is interesting that the Bi(III)/Bi(V) manifold operates fluorination whereas the Bi(I)/Bi(III) manifold can drive defluorination of polyfluoroarenes. These two catalytic reactions explicitly exemplify that both catalytic oxidative and reductive chemistry can be achieved by employing relevant Bi redox couples.

The tethered bis-aryl ligand platform bearing a pendant neutral ligand was further exploited in an oxidative coupling of arylboronic acids with perfluoroalkyl sulfonate salts (Figure 11A). A related stoichiometric reaction was previously reported by Mukaiyama, in which a stoichiometric oxidative coupling between phenylbismuthine species and an excess of triflic acid in the presence of m-chloroperoxybenzoic acid (mCPBA) gives phenyl triflate 82 in 29% yield. This reductive elimination type reaction was advanced into Bi-catalyzed triflation and nonafluoroboration of aryloboronic acids using the corresponding perfluoroalkyl sulfonate salts. In this catalysis, a modified Bi(III) catalyst 76 ligated with bis(m-
tri fluoromethyl-phenyl) sulfone is used. A more electron-deficient backbone is introduced to render the Bi(III) a better leaving group during C—O bond formation. Indeed, Bi(III) catalysts 76 and 77 (10 mol %) drive triflation and nonaflation of aryl boronic acids, respectively, in the presence of a perfluoroalkyl sulfonate salt (NaOTf or KONf, 1.1 equiv), an oxidant 67 (1.1 equiv), and Na3PO4 (2 equiv). This method accommodates aryl boronic acids with various types of substitution (82−91).

Analogous to the fluorination catalyzed by 63, the Bi(III) catalyst (76 or 77) is proposed to undergo transmetalation and reductive elimination via a Bi(V) intermediate.

Given that triflate and nonaflate are highly electronegative, poorly nucleophilic, and weakly coordinating, C—O bond formation is inherently challenging using TM complexes and a few chemistry is known for triflation steps by transition metals. As revealed in fluorination catalysis, this oxidative coupling reaction via a Bi(III)/Bi(V) cycle has also enabled new transformations that are relatively challenging in TM catalysis by taking advantage of the unique reactivity of bismuth complexes.

4. REDOX-NEUTRAL Bi(III) CATALYSIS

While non-redox Bi catalysis has been dominated by Lewis acid catalyzed transformations, redox-neutral Bi(III) catalysis in which a Bi(III) catalyst does not act as a mere Lewis acid has been recently demonstrated in a catalytic synthesis of (hetero)aryl sulfonyl fluorides from (hetero)aryl boronic acids using sulfur dioxide (SO2) and Selectfluor (96) (Figure 12).74 A Bi(III) catalyst 92 was found to be an optimal catalyst for triflation and nonaflation of aryl boronic acids. (B) Proposed mechanism via a Bi(III)/Bi(V) cycle. (C) Validation of elementary steps including transmetalation and reductive elimination via a Bi(V) intermediate.
this reaction, which was discovered through modification of the diarylsulfone ligands that were used in Bi(III)/Bi(V) redox catalysis. Analogous to the fluorination and the triflation catalysis (section 3), the catalyst 92 readily undergoes transmetallation with a (hetero)aryl boronic acid to generate (hetero)arylbismuthine 94. Although stoichiometric reactivities of both Bi(III)−C75 and Bi(V)−C76 toward SO2 or its surrogates have been known, it was found that Bi(III) intermediate 94 is an active species for the insertion of SO2 into the Bi−C bond which gives a diarylbismuth sulfinate 95. Upon oxidation by electrophilic fluorine source, complex 95 then affords the corresponding (hetero)aryl sulfonyl fluoride with regeneration of catalytically active Bi(III) species 93. In this catalytic reaction, it was demonstrated that the oxidant (96) does not oxidize the Bi center but the S(IV) to form the S−F bond. Thus, unlike aforementioned Bi(III)/Bi(V) redox catalysis, this reaction does not involve Bi(V) intermediates, achieving a redox-neutral Bi(III) catalysis with an insertion step. This method can tolerate various functional groups (97−102). In addition, by using a milder oxidant, N-fluorobenzensulfonimide (NFSI), instead of 96, heteroaryl boronic acids can be tolerated (103−106), which has been challenging for Bi catalysis using strong oxidants. Compared to related two-step sequence TM-catalyzed reactions,77 Bi catalysis provides a convenient and competent synthetic method for sulfonyl fluorides with high functional group compatibility.

5. CONCLUSIONS AND FUTURE OUTLOOK

In this Perspective, we provided an overview of recent efforts to leverage the Bi(II)/Bi(III), Bi(I)/Bi(III), and Bi(III)/Bi(V) redox couples for discovery of new reactivity and development of new main group catalysts. It is clear that the field of bismuth redox catalysis is still in its infancy, yet it has provided compelling evidence that new applications are awaiting in the area of organic synthesis, which could certainly reach beyond those catalyzed by transition metals. Looking ahead, we anticipate numerous opportunities for discovery in bismuth redox catalysis:

(1) While other elementary steps (e.g., OA, LM, RE) comprising TM catalysis are analogously realized in Bi catalysis, combinations with migratory insertion-type elementary steps are relatively less explored.28,49,57−59,67−69 Incorporating this type of insertion step into a catalytic cycle would enable new transformations, using small molecules as building blocks.

(2) Compared to organo−Bi(I), −Bi(III), and −Bi(V) compounds, open-shell −Bi(0), −Bi(II), and −Bi(IV) species are much less explored or unknown.70 These species might provide further opportunities to unveil new catalytic cycles and reaction pathways. For example, dual photoredox/bismuth catalysis or combined electrochemistry with bismuth, could be envisioned to precisely control oxidation or reduction of bismuth complexes and ultimately enable selective or challenging transformations.

(3) Combined with diverse redox catalysis and the robust nature of Bi complexes, development of molecular Bi-based electrocatalysts is feasible, which could provide better understanding in heterogeneous electrocatalysis at the molecular level.82

(4) Given the orthogonal or complementary reactivity of Bi catalysts, Bi redox cycles could be merged with TM catalysis to achieve challenging transformations via dual Bi/TM catalysis.

(5) In more-complex settings, stereoselective redox transformations or bioconjugation reactions could be devised for organobismuth complexes, because of the facile introduction of chiral elements around its Bi center, and their benign nature and stability in aqueous solutions, respectively.

(6) Finally, dinuclear or multinuclear complexes with mixed oxidation states would also allow one to discover new redox chemistry.80

We hope that this Perspective will draw more attention to the infant field of redox catalysis using bismuth, provide guiding principles for new advancements in catalysis and synthesis, and promote realization of the full potential of such a new area of expertise.

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