Kobe University Repository : Kernel

PDF issue: 2026-02-08

Multifaceted reactivity of benzimidazoline as an electron donor, a hydride donor, and a catalyst

Harada, Tatsuhiro
Murakami, Suguru
Matsubara, Ryosuke

(Citation)
Tetrahedron Chem,16:100147

(Issue Date)
2025-12

(Resource Type)
journal article

(Version)
Version of Record

(Rights)
© 2025 The Authors. Published by Elsevier Ltd.
This is an open access article under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International license

(URL)
https://hdl.handle.net/20.500.14094/0100498929

Tetrahedron Chem 16 (2025) 100147

Contents lists available at ScienceDirect

Tetrahedron Chem

journal homepage: www.journals.elsevier.com/tetrahedron-chem

Multifaceted reactivity of benzimidazoline as an electron donor, a hydride donor, and a catalyst

Tatsuhiro Harada, Suguru Murakami [*], Ryosuke Matsubara [**]

Department of Chemistry, Graduate School of Science, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe, 657-8501, Japan

A R T I C L E I N F O

Keywords:
Benzimidazoline
Organic hydride donor
Hydride transfer
Electron transfer
Photochemical regeneration
CO_2 reduction
Sustainable catalysis

A B S T R A C T

Organic hydrides are metal-free, sustainable reductants with broad structural diversity and tunable reactivity. Among them, 1,3-dimethylbenzimidazoline (BIH) stands out as one of the most potent C–H-based reducing agents. This review highlights the distinct properties of BIH that enable its versatile functionality as a hydride, electron, and hydrogen atom donor and summarizes its stoichiometric and catalytic applications in organic synthesis and CO_2 reduction. Recent advances in BIH regeneration strategies based on chemical, electrochemical, and photochemical methods are also discussed, emphasizing their relevance to sustainable catalysis. Particular attention has been paid to photochemical regeneration systems that enable visible light-driven catalytic cycles, including photosensitizer-free systems. These insights provide a foundation for the future development of BIH-based redox systems within green and efficient synthetic methodologies.

1. Introduction

Organic hydrides are a class of reductants that has been increasingly studied in recent years. They are broadly defined as metal-free organic molecules capable of donating electrons. Although metal hydride species play various important roles in synthetic chemistry, their reliance on scarce transition metals, especially Rh and Ru, poses a significant sustainability challenge [1]. In contrast, organic hydrides, comprising abundant elements such as carbon and nitrogen, offer a more sustainable alternative. An additional advantage of organic hydrides is that the structural diversity of organic molecules allows for broader designability and optimization.

The simplest strategy for enabling hydrogen to function as a hydride is to bond it to an element that is more electropositive than itself (Fig. 1). Boron and silicon, which form borohydrides and hydrosilanes, respectively, are two such elements typically used to generate organic hydrides. Sodium borohydride ($NaBH_4$) is among the most widely used non-metal hydrides for reducing carbonyl groups to alcohols. In certain cases, however, a hydrogen atom can function as a hydride even when bonded to a more electronegative element. The biological reductant, nicotinamide adenine dinucleotide phosphate (NADPH), donates a hydride via C–H bond dissociation. This process is driven by the electron-donation of the nitrogen lone pair that is π-conjugated with the C–H bond undergoing cleavage and aromatization stabilization. Artificially synthesized Hantzsch esters, which mimic the dihydropyridine skeleton of NADPH, are often used as sacrificial electron donors or photo-activated reductants [2–4].

Extending this concept, increasing the number of electron-donating nitrogen atoms from one to two is expected to deliver stronger reductants than dihydropyridine derivatives. Indeed, 1,3-dimethylbenzimidazoline (BIH), which contains two nitrogen atoms conjugated with the C–H bond undergoing cleavage, is one of the strongest reductants among isolable C–H hydrides. The oxidation of **2-R-BIH** (BIH bearing substituent (R) at the 2-position), involving the transfer of two electrons and one proton, yields **2-R-BI**$^+$ (1,3-dimethylbenzimidazolium (BI$^+$) bearing substituent (R) at the 2-position). Owing to the high aromatic stability of **2-R-BI**$^+$ and its resistance to decomposition, the process is fully reversible, allowing **2-R-BI**$^+$ to be efficiently regenerated to **2-R-BIH** via various methods (Fig. 2) [5]. Therefore, BIH is, in principle, a powerful reductant that can function catalytically. These advantageous characteristics have prompted significant research centered on various BIH analogues [6].

Focusing on the excellent electron- and hydride-donating abilities of BIH, this review summarizes seminal studies as well as selected recent examples of its application in organic synthesis. Furthermore, the quantification of the reducing capacity of BIH is briefly discussed, as

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: murakami.suguru@harbor.kobe-u.ac.jp (S. Murakami), matsubara.ryosuke@people.kobe-u.ac.jp (R. Matsubara).

https://doi.org/10.1016/j.tchem.2025.100147
Received 12 August 2025; Received in revised form 2 September 2025; Accepted 12 September 2025
Available online 17 September 2025
2666-951X/© 2025 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

well as the synthetic methods for its formation, providing a guideline for the development of new reactions based on BIH.

2. Quantifying the reducing capacity of BIH

Quantifying the reducing strength of organic hydrides is important for rational reaction development. Methods for quantifying and comparing the reducing abilities of organic hydrides are discussed below.

Fig. 3(a) depicts the case wherein two electrons and one proton are donated simultaneously as a hydride. Hydricity, which refers to the ability of a molecule to donate a hydride, is governed by both thermodynamics and kinetics.

The thermodynamic hydricity can be evaluated by examining the Gibbs energy change associated with the dissociation of a hydride donor (R–H) into a hydride acceptor (R^+) and hydride anion (H^-) (Eq. (1)).

$$R-H \rightarrow R^+ + H^-$$

$$\Delta G_{H^-} = G(R^+) - G(R-H) + G(H^-) \qquad \text{[Eq. 1]}$$

Although the thermodynamic hydricity (ΔG_{H^-}) of several systems has been determined experimentally [7–9], the convenience and progressive accuracy of quantum chemical calculations have made this the preferred approach estimating in recent years. However, calculating the Gibbs energy of the hydride ion G (H^-) accurately remains a significant challenge. To address this issue, Muckerman et al. proposed a method based on the correlation between experimental thermodynamic hydricity values and calculated Gibbs energies [10]. When ΔG_{HHR} is defined as the difference between G (R^+) and G (R–H) (Eq. (2)), then from Eqs. (1) and (2), ΔG_{H^-} is proportional to ΔG_{HHR} with a slope of 1 and an intercept corresponding to G (H^-) (Eq. (3)). Applying this relation, they plotted the calculated ΔG_{HHR} and experimentally measured ΔG_{H^-} values of five hydride compounds (Fig. 4(a)). Using the resulting correlation equation and calculated ΔG_{HHR} values of various hydride compounds, they accurately predicted the corresponding experimental thermodynamic hydricities (Fig. 4(b)).

$$\Delta G_{HHR} = G(R^+) - G(R-H) \qquad \text{[Eq. 2]}$$

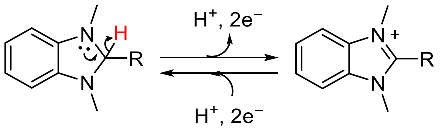
$$\Delta G_{H^-} = \Delta G_{HHR} + G(H^-) \qquad \text{[Eq. 3]}$$

Inspired by this work, Ilic et al. compiled the reported experimental and calculated thermodynamic hydricity values for over 200 metal-free hydrides [11] and further evaluated the hydricity of various compounds, particularly in the context of CO_2 reduction [12–14]. Their studies highlighted the superior thermodynamic hydricity of BIH compared to those of acridine- and pyridine-based hydrides.

On the other hand, kinetic hydricity can be determined by analyzing the reaction rate of hydride transfer.

$$k = s(N + E) \qquad \text{[Eq. 4]}$$

Mayr et al. proposed Eq. (4), which describes the rate constant of a polar reaction (k) as a function of the nucleophilic reactivity parameter (N), electrophilic reactivity parameter (E), and slope factor (s) [15]. Here, the kinetic hydricity corresponds to the nucleophilicity parameter N. Using this relation, the N values of various organic hydrides, including hydrocarbons [16], hydrosilanes [14], borohydrides [17], dihydropyridines [17], and BIH [18] were calculated. According to their results, BIH derivatives displayed the highest N values among the investigated C–H hydrides, being comparable to those of hydrostannanes (Fig. 5).



2-R-BIH **2-R-BI+**

Fig. 2. BIH as a recoverable electron donor.

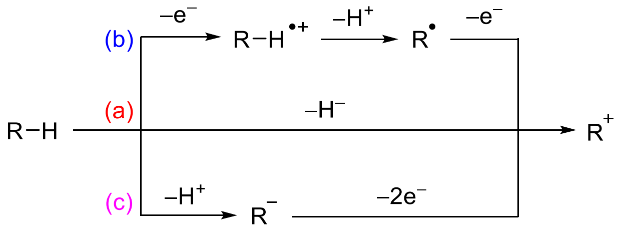


Fig. 3. Mechanistic pathways via which organic hydrides donate electrons.

Next, we considered the scenario wherein an organic hydride donates electrons in a stepwise manner (Fig. 3(b)). The electron-donating ability of a compound is governed by its oxidation potential, which can be experimentally determined using cyclic voltammetry. The oxidation potential of BIH is approximately +0.3 V vs. SCE [19], which is considerably lower than that of commonly used sacrificial electron donors such as aliphatic amines (+0.8–1.0 V vs. SCE [20]). Therefore, in addition to its hydride donor functionality, BIH can also serve as an efficient single-electron donor. Single electron donation generates the $BIH^{•+}$ species, which undergoes deprotonation under basic conditions (pK_a ~12–15 [21]) to form $BI^•$. The $BI^•$ radical species is open-shelled and its reducing strength (E_{red} ~ −1.7 V vs. SCE for BI^+ [22]) is significantly higher than that of BIH; thus, it readily donates a second electron to generate BI^+. Both BIH and $BIH^{•+}$ can also donate an electron and a proton, thereby acting as a hydrogen atom donor.

In principle, organic hydrides can undergo proton transfer as the initial step, followed by electron transfer (Fig. 3(c)). However, reduction via this pathway is rare because the extremely high pK_a values (35–50 [21]) of most organic hydrides preclude initial proton transfer, except under highly basic conditions.

3. Synthesis of BIH and BI^+

Two general synthetic strategies have been adopted for accessing BIH and its oxidized form BI^+, as illustrated in Fig. 6. Both approaches utilize readily available *o*-phenylenediamine as the starting material, each employing a distinct sequence of oxidation and reduction steps.

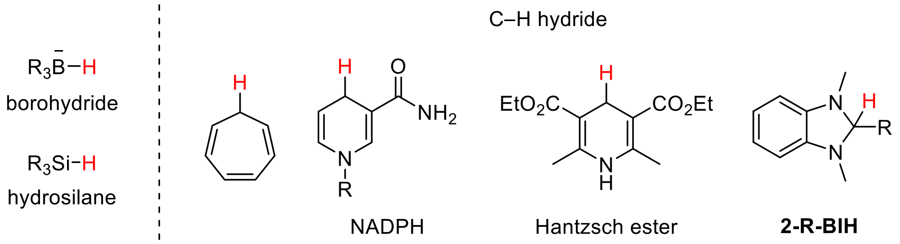


Fig. 1. Various organic hydrides.

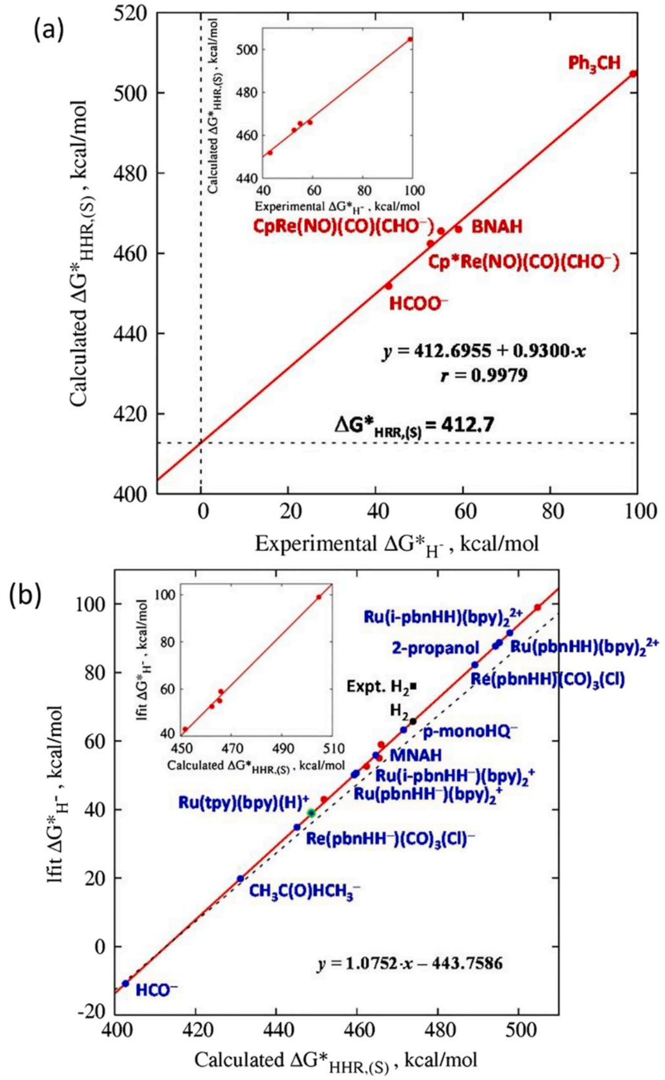


Fig. 4. Muckerman's approach for predicting thermodynamic hydricity. Reproduced from Ref. [10].

3.1. Route (a): synthesis of BIH via BI$^+$

In this route, synthesis begins with the formation of a benzimidazole scaffold via the condensation of *o*-phenylenediamine with a carboxylic acid [23] or an aldehyde. When an aldehyde is used, an additional oxidant such as air [24], sodium metabisulfite ($Na_2S_2O_5$) [25], and sodium bisulfite ($NaHSO_3$) [26] is required to facilitate cyclization and aromatization. The resulting benzimidazole is then methylated to yield the cationic species **2-R-BI**$^+$ [27–29]. Finally, **2-R-BI**$^+$ can be efficiently reduced to **2-R-BIH** using $NaBH_4$ [29].

3.2. Route (b): synthesis of BI$^+$ via BIH

The alternative pathway relies on *N,N*′-dimethyl-*o*-phenylenediamine as the key intermediate [30,31]. Its preparation from *o*-phenylenediamine typically entails sequential tosyl protection of the amine groups, methylation, and deprotection to ensure monomethylation of the amines. The resulting dimethylated diamine is then condensed with an aldehyde to form **2-R-BIH** directly [19]. Oxidation of **2-R-BIH** with iodine (I_2) [32], 2-bromoacetophenone [33], or other suitable oxidants yields **2-R-BI**$^+$.

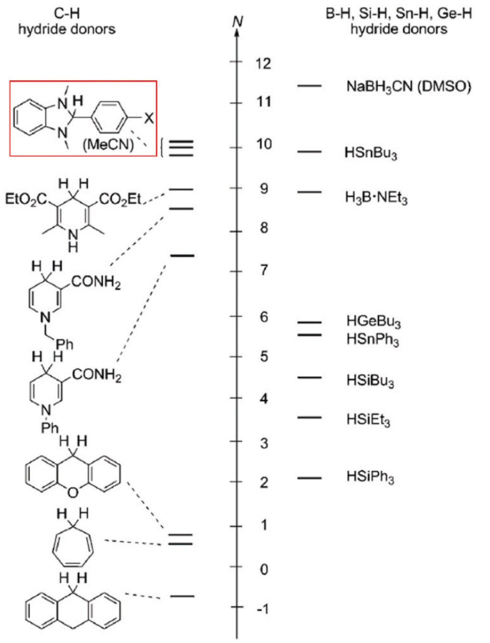


Fig. 5. Comparison of the nucleophilic parameter *N* values of various hydride donors. Adapted from Ref. [18].

3.3. Counterion considerations

Iodide is the most commonly used counter ion for BI because of its availability and compatibility with various synthetic protocols. However, there are concerns associated with its use, such as the potential for heavy-atom effects, which shorten the lifetime of the singlet excited state, and its susceptibility to one-electron oxidation. To address these concerns and expand the scope of BI$^+$ applications, alternative counterions such as sulfonates [34] and perchlorates [35,36] have been explored.

4. Application of BIH in organic reactions

4.1. Stoichiometric use of BIH as a reductant

BIH was initially applied in organic reactions as a stoichiometric hydride source. Chikasita et al. demonstrated the utility of **2-Ph-BIH** as a hydride source for the reduction of α-haloacetophenones (Fig. 7) [37]. They observed that sterically hindered substrates exhibited lower reactivities, suggesting that the reduction of carbonyl compounds proceeded via an S_N2 reaction mechanism. Stereochemical inversion of the substrate was observed, providing further evidence for the hydride transfer mechanism illustrated in Fig. 3(a).

The BIH reduction mechanism is dependent on the electrophilicity of the substrate. Tanner et al. [38] reported the reduction of α-nitrosulfones to nitroalkanes via a mechanism involving single-electron transfer (SET) and hydrogen-atom transfer (HAT) (Fig. 8). In this process, the highly electrophilic α-nitrosulfones accept an electron from **2-Ph-BIH**, forming a nitrosulfone radical anion. This intermediate then undergoes fragmentation to produce a nitroalkane radical and a sulfonate leaving group. Subsequently, the nitroalkane radical abstracts a hydrogen atom from another BIH molecule to produce the desired nitroalkanes and BI$^\bullet$. The resulting BI$^\bullet$ species can transfer an electron to another substrate, thereby propagating the reduction cycle.

Thermal reduction using BIH requires highly electrophilic substrates such as-α-halocarbonyl compounds and-α-nitrosulfones. However, this limitation can be overcome through photochemical activation. Generally, photoexcited molecules exhibit enhanced electron-accepting abilities, thereby enabling electron transfer from BIH to a broader range of

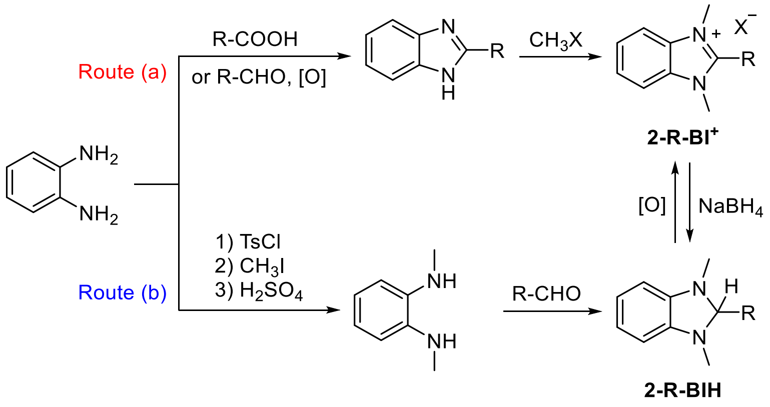


Fig. 6. Representative synthetic routes to BI$^+$ and BIH starting from *o*-phenylenediamine.

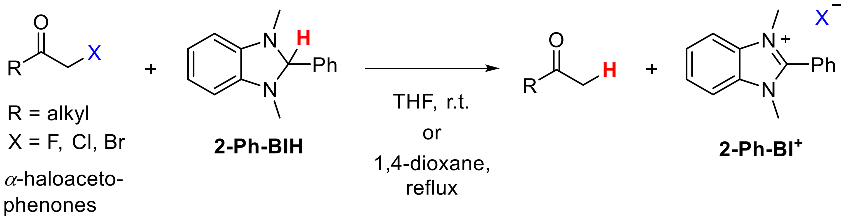


Fig. 7. Reduction of α-halocarbonyl compounds using BIH as a stoichiometric hydride source.

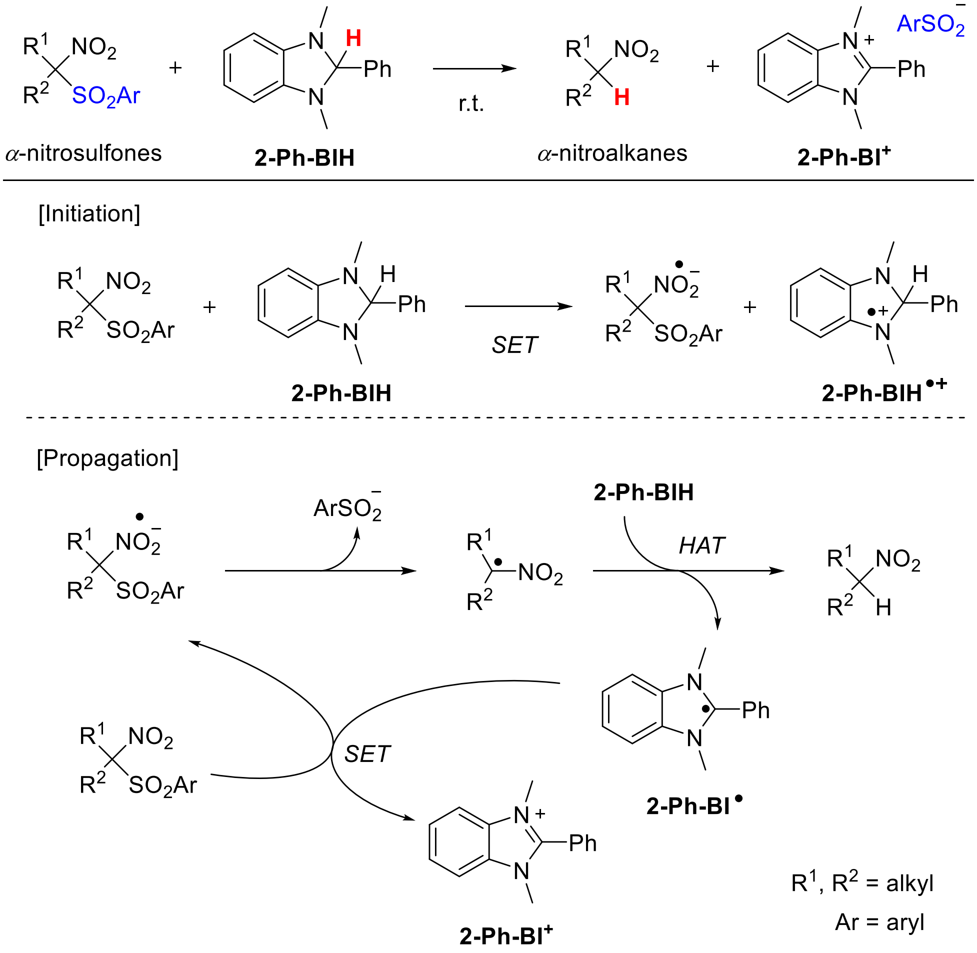


Fig. 8. BIH-mediated reduction of α-nitrosulfones to nitroalkanes.

substrates. Hasegawa et al. first demonstrated the use of BIH as an electron donor in a photoreduction reaction [39]. Specifically, the reduction of *α*,*β*-epoxyketones was achieved under irradiation with a Xe−Hg lamp (Fig. 9). Upon excitation, the *α*,*β*-epoxyketone accepts an electron from **2-Ph-BIH**, forming a ketyl radical. This intermediate then undergoes ring opening, followed by protonation to yield either an alkoxy or a *β*-keto radical. Finally, these radical species are reduced by **2-Ph-BI•**, and the resulting intermediates are protonated to afford the corresponding *β*-hydroxyketone.

Building on previous studies wherein BIH was employed as a reductant in photoinduced electron transfer reactions, its application to CO_2 reduction as a synthetic analog of NADPH, represents a logical extension of its reductive utility. The principal goal of artificial photosynthesis is the conversion of CO_2 into value-added chemicals, such as CO, formic acid, and methanol, which ultimately enables the storage of solar energy in chemical bonds. Ishitani and Koike et al. developed a BIH-mediated photocatalytic system for CO_2 reduction to CO using a Ru−Re bridged complex and visible-light irradiation (Fig. 10) [40]. A key advantage of BIH in such systems is the behavior of its radical intermediates. In previous studies [41], 1-benzyl-1,4-dihydronicotinamide (BNAH) was employed as a reductant in a similar CO_2 reduction process; however, the corresponding radical species generated via one-electron oxidation and subsequent deprotonation readily undergoes dimerization. This side reaction limits the ability of BNAH to function as a true two-electron donor. In contrast, dimerization of the radical intermediate derived from BIH (BI•) is unfavored; therefore, sequential electron transfer is the dominant process. Thus, the development of photocatalytic systems that utilize BIH derivatives as effective two-electron reductants is anticipated.

The selective conversion of CO_2 to formate via transition metal catalysis remains a significant challenge, primarily because of the competing side reactions that produce CO and/or H_2. Musgrave and Lim et al. developed a CO_2 reduction system for selective formate production utilizing **2-Me-BIH** as a stoichiometric hydride donor (Fig. 11) [42]. The optimal system conditions entailed slightly pressurized CO_2, elevated temperatures, and the presence of a large excess of metal salts. Notably, the reaction proceeded without any catalyst or external energy input such as electricity or light irradiation. They evaluated the effectiveness of the hydride transfer from BIH to CO_2 based on DFT calculations of the transition state. A lower Gibbs energy barrier was correlated with a higher yield of formate, indicating that hydride transfer efficiency plays a critical role in the reaction outcome. Moreover, they successfully regenerated BIH from BI^+ via an electrochemical process. However, a catalytic CO_2 reduction system enabled by the electrochemical regeneration of BIH has not yet been developed. Nonetheless, achieving CO_2 reduction without the use of transition metals, along with the potential for electrochemical regeneration of the hydride donor, represents a significant advancement. Overall, this approach offers a promising platform toward sustainable fuel production via solar energy conversion.

Although BIH is a promising hydride source for the reduction of CO_2 to formate, its high kinetic barrier limits the overall reaction efficiency. Glusac et al. investigated self-exchange reorganization energies using the Marcus theory, combining DFT calculations and kinetic experiments [13]. Their findings indicate that even in the case of an ideal BIH-based hydride donor, hydride transfer would proceed with slow kinetics, resulting in fewer than 100 turnovers per second under a driving force (ΔG° for hydride transfer to CO_2) of −0.1 eV. This limitation accounts for the long reaction time (11–24 h) applied in the system shown in Fig. 11. Based on these insights, they proposed that a stepwise mechanism involving the separate transfer of electrons and protons to CO_2 may be more effective for formate production than the conventional hydride

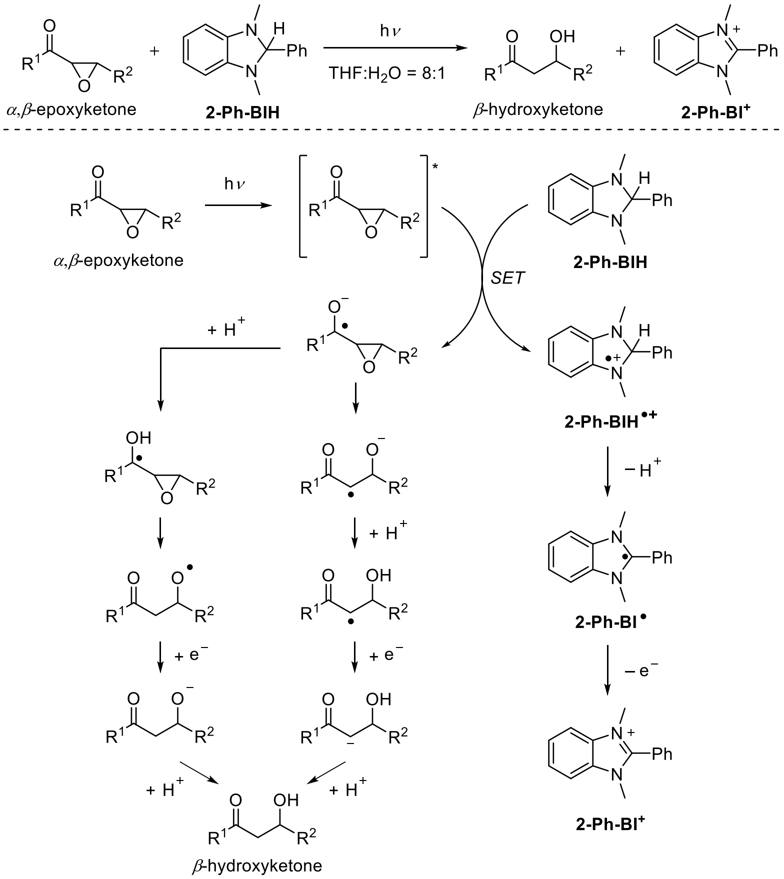


Fig. 9. Photochemical reduction of *α*,*β*-epoxyketone to *β*-hydroxyketone using BIH as an electron donor.

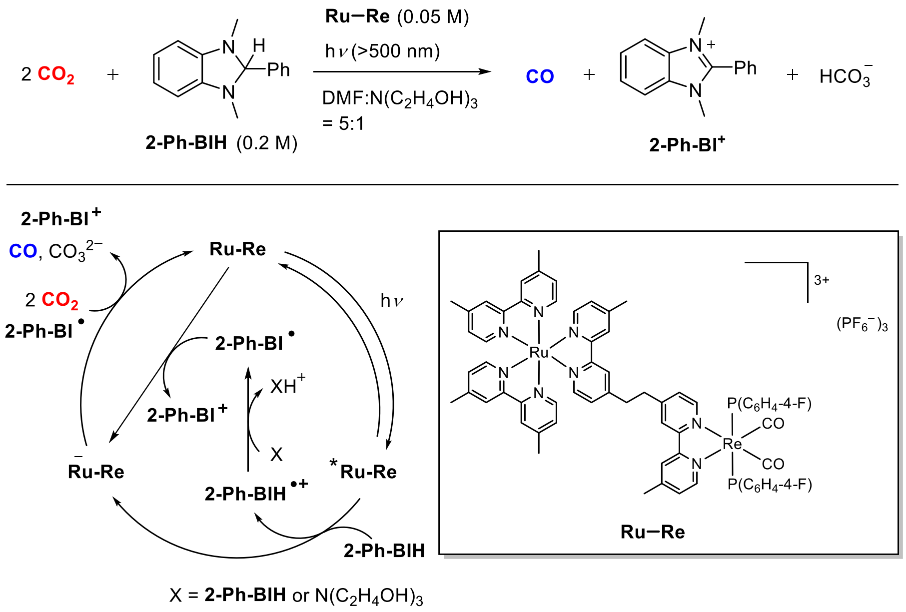


Fig. 10. Photocatalytic CO_2 reduction using BIH as a stoichiometric reductant.

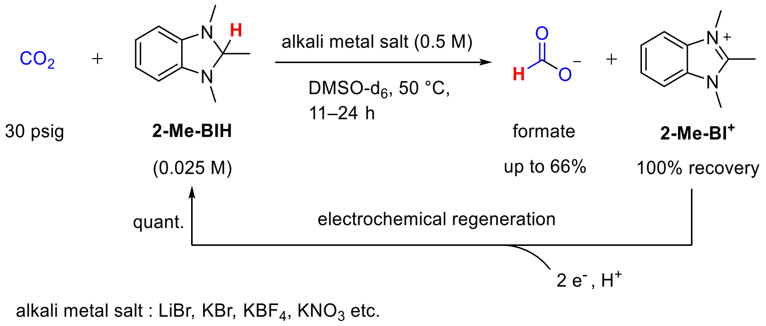


Fig. 11. CO_2 reduction to formate using BIH and electrochemical regeneration thereof.

transfer pathway.

4.2. Catalytic use of BIH as an electron donor

From environmental and efficiency considerations, the structural design of organic hydrides should be as simple as possible, especially when they are used in stoichiometric amounts. Large-scale syntheses of complex organic hydrides are time-consuming and require significant quantities of solvents, reagents, and energy. Therefore, it is essential to develop organic hydride regeneration methods using inexpensive reducing agents.

One of the most straightforward methods for regenerating BIH from BI^+ is via reduction by $NaBH_4$, as illustrated in Fig. 6. Tuttle and Murphy et al. reported a regeneration method that proceeds via reductive radical cyclization, wherein $NaBH_4$ serves as a sacrificial reductant and **2-H-BIH** as a catalyst (Fig. 12) [43]. In this system, BIH donates two electrons and one proton to the substrate, and is subsequently regenerated in situ by $NaBH_4$.

Hasegawa et al. developed photochemical desulfonylation reactions [36,44] and desulfonylative Truce-Smiles rearrangements [45] using **2-Ar-BIH** compounds (Ar = naphthoxy, pyrenyl, anthryl, diarylaminophenyl, etc.) as photocatalysts and $NaBH_4$ or pic-BH_3 as sacrificial reductants (Fig. 13). The incorporation of a chromophore at the 2-position of these BIH derivatives enabled them to function as highly potent electron donors upon visible light excitation.

In the above reactions, the conversion of BI^+ to BIH is effected by the chemical energy provided by $NaBH_4$. Alternatively, other energy sources, such as electricity and light, can be employed for this transformation. Glusac et al. reported the electrochemical regeneration of BIH [21]. They demonstrated that BIH regeneration proceeds via a

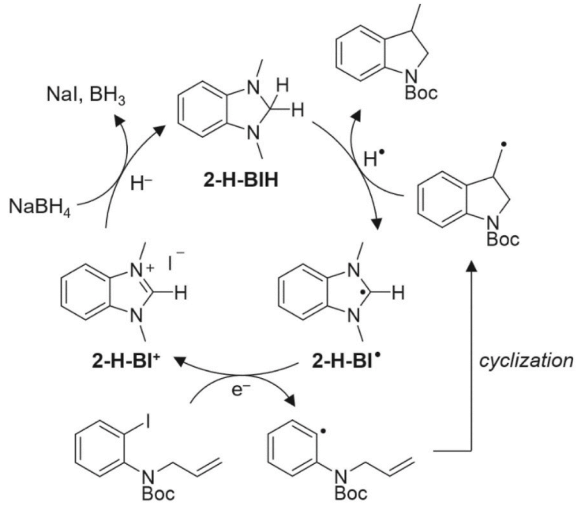


Fig. 12. Mechanism of the thermal reduction reaction catalyzed by BIH reported by Tuttle and Murphy et al. [43].

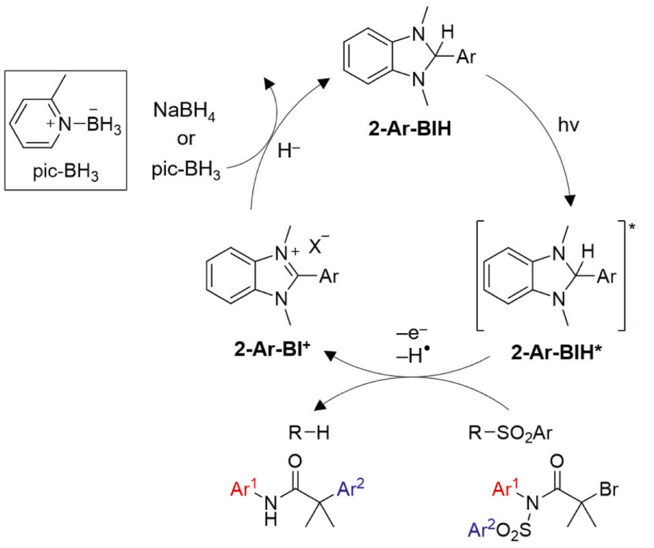


Fig. 13. The application of BIH derivatives as photocatalysts in photochemical reduction reactions, reported by Hasegawa et al.

sequential electron-electron-proton transfer (EEP) pathway (reverse of Fig. 3(c)) under neutral conditions, or via a sequential electron-proton-electron transfer (EPE) pathway (reverse of Fig. 3(b)) in the presence of acetic acid (Fig. 14). BI$^\bullet$ is readily protonated, even by weak acids such as acetic acid, owing to its relatively high basicity (the pK_a of its conjugate acid, BIH$^{\bullet+}$ is approximately 12). In contrast, the basicity of radicals derived from acridine- or phenanthridine-based hydrides is very low (pK_a < 2); therefore, the EEP pathway is favored unless a very strong acid, such as triflic acid, is present. The preference for the EPE pathway is a unique characteristic of BIH.

Light energy is a sustainable resource readily harvested from sunlight, the most intense component of which is visible light [46]. Therefore, visible light is an important energy source. Although electricity can be generated from light, the direct utilization of light is vastly more efficient.

Glusac et al. reported the photochemical regeneration of BIH using phenazine-based photosensitizers, thiolate as the sacrificial electron donor, and phenol as the proton source (Fig. 15) [47]. In this reaction, upon excitation by visible light, the photosensitizer donates an electron to BI$^+$, enabling its regeneration (Note: A “photosensitizer” is generally defined as a substance that, upon light excitation, transfers only energy or electrons. Although the term “photocatalyst” is sometimes used interchangeably with “photosensitizer”, it is also explicitly distinguished when referring to a substance that transfers atoms. In the present review, we adhered to this distinction).

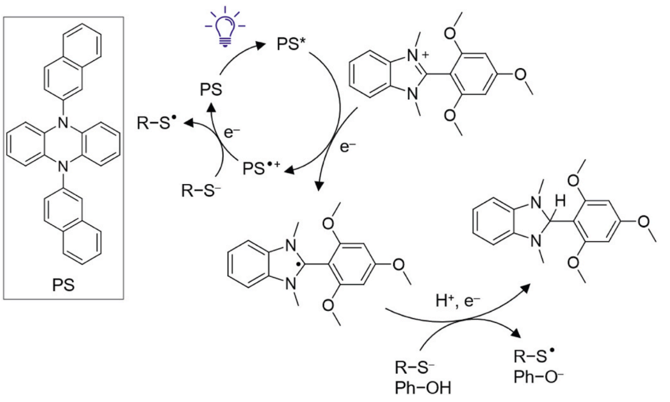


Fig. 15. Mechanism of photochemical BIH regeneration reported by Glusac et al. [47].

Around the same time, Yamanaka, Kobori, and Matsubara et al. reported a photocatalytic CO$_2$ reduction reaction encompassing the photochemical regeneration of BIH by the photosensitizer (Fig. 16) [48]. In this system, the carbazole-based photosensitizer plays a dual role: first, it reduces CO$_2$ to the CO$_2$ radical anion; second, it regenerates BIH, which acts as a hydrogen atom transfer catalyst. BIH then further reduces the CO$_2$ radical anion to formate. This stepwise reduction process avoids the kinetic limitations associated with direct hydride transfer, as discussed in Section 4.1. This work represents the first example of a catalytic reaction proceeding via an in situ photochemical regeneration of BIH. Moreover, a significant decrease in the formate yield was observed when BIH was used as the sacrificial reductant instead of ascorbic acid. This phenomenon was attributed to the quenching of the photosensitizer by BI$^+$, which leads to the dissipation of light energy. Thus, the use of BIH in catalytic amounts proved essential for maximizing yields.

Matsubara et al. explored the possibility of eliminating photosensitizers from photochemical regeneration systems using BI$^+$ derivatives capable of absorbing visible light. They discovered that BI$^+$ derivatives bearing dimethylaminophenyl groups can undergo direct photochemical regeneration under visible-light irradiation without the need for a photosensitizer (Fig. 17) [22]. These derivatives exhibit visible-light absorption in contrast to **2-Ph-BI**$^+$, which absorbs light only in the ultraviolet region. The HOMO and LUMO were determined to be predominantly localized over the 2-aryl and BI$^+$ moieties, respectively, indicating that intramolecular charge transfer contributed to the absorbance wavelength extension (Fig. 18). The photoexcited BI$^+$ species feature sufficiently high reduction potentials to accept an electron, and the calculated activation energy for the subsequent hydrogen atom transfer from ascorbic acid is sufficiently low ($\Delta G^{\ddagger} = 15.2$ kcal mol^{-1}) to

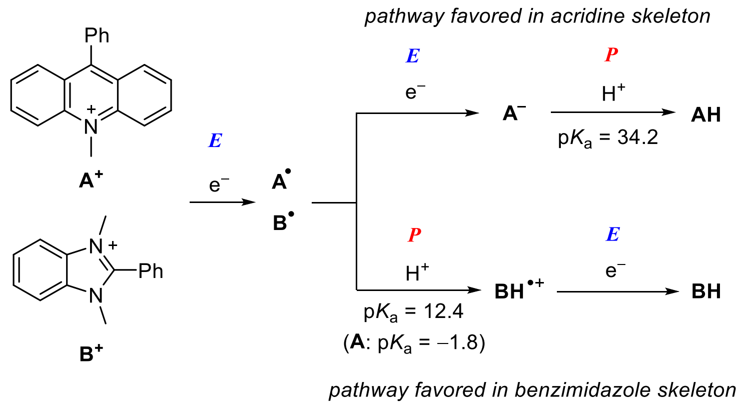


Fig. 14. Two possible pathways for the electrochemical regeneration of organic hydrides Values were calculated in Ref. [21].

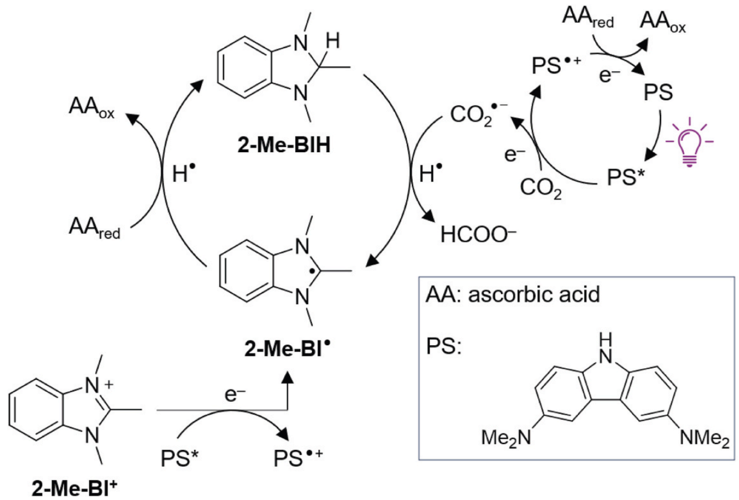


Fig. 16. BIH-catalyzed photochemical CO_2 reduction reported by Yamanaka, Kobori, and Matsubara et al. [48].

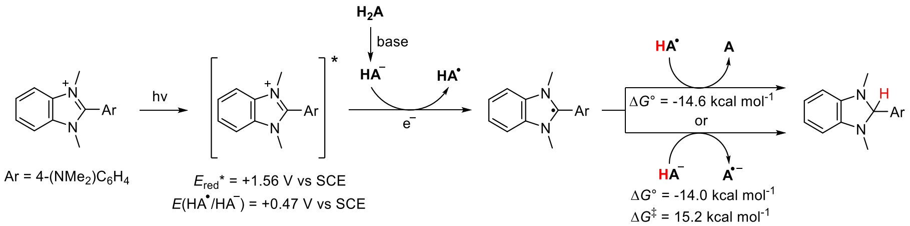


Fig. 17. Photochemical regeneration of BIH under visible-light irradiation without the involvement of a photosensitizer. Adapted from Ref. [22].

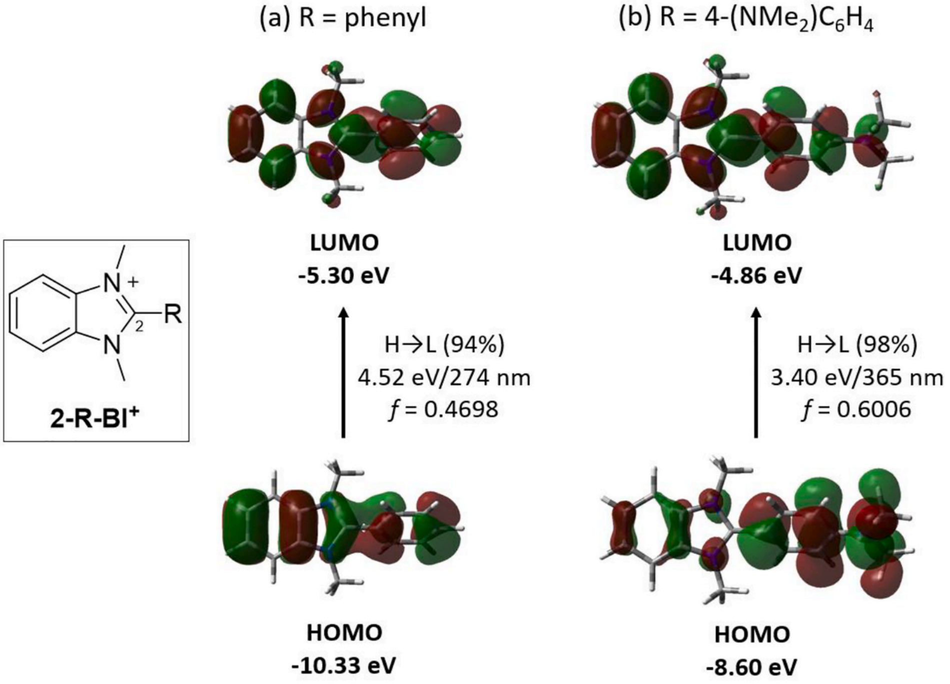


Fig. 18. Rationale for the red-shifted absorption of **2-R-BI**$^+$. Adapted from Ref. [22]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

allow the reaction to proceed at room temperature.

5. Conclusions

Organic hydrides represent a promising class of reductants for the advancement of sustainable chemistry, and BIH embodies its potential through its strong reducing ability, stability, and structural diversity. In this review, we outlined the distinct properties of BIH that enable its versatile functionality as a hydride, electron, and hydrogen atom donor with a particular focus on its application in CO_2 reduction, which is a reaction of major environmental significance. Although the direct hydride transfer from BIH to CO_2 remains kinetically sluggish, catalytic strategies involving stepwise electron/proton transfer and photochemical activation are promising. Furthermore, the regeneration of BIH from BI^+ via chemical, electrochemical, and photochemical processes enables its use in catalytic cycles, leading to reduced waste and improved efficiency. The development of photosensitizer-free photochemical regeneration systems enhances the sustainability of BIH-based redox processes. As the global demand for green chemical technologies continues to increase, the catalytic use of BIH as a central component of organohydride-based systems is likely to attract increasing interest.

CRediT authorship contribution statement

Tatsuhiro Harada: Writing – original draft, Funding acquisition, Conceptualization. **Suguru Murakami:** Writing – original draft, Funding acquisition, Conceptualization. **Ryosuke Matsubara:** Writing – original draft, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ryosuke Matsubara reports financial support was provided by JSPS. Ryosuke Matsubara reports financial support was provided by Shiraishi Foundation of Science Development. Ryosuke Matsubara reports financial support was provided by NORITZ Nukumori Foundation. Suguru Murakami reports financial support was provided by JSPS. Tatsuhiro Harada reports financial support was provided by JST. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by JSPS KAKENHI (JP25K18036, JP24K01487, JP23H03961), JST SPRING (JPMJSP2148), Shiraishi Foundation of Science Development, and NORITZ Nukumori Foundation (RS2313, RS2407).

Data availability

Data will be made available on request.

References

[1] M.L.C.M. Henckens, P.P.J. Driessen, E. Worrell, Metal scarcity and sustainability, analyzing the necessity to reduce the extraction of scarce metals, Resour. Conserv. Recycl. 93 (2014) 1–8, https://doi.org/10.1016/j.resconrec.2014.09.012.
[2] J.W. Yang, M.T. Hechavarria Fonseca, B. List, A metal-free transfer hydrogenation: organocatalytic conjugate reduction of alpha,beta-unsaturated aldehydes, Angew. Chem. Int. Ed Engl. 43 (2004) 6660–6662, https://doi.org/10.1002/anie.200461816.
[3] M.-M. Zhang, S.-H. Li, J.-L. Tu, Q.-Q. Min, F. Liu, Metal-free iminyl radical-mediated C–C single bond cleavage/functionalization of redox-active oxime esters, Org. Chem. Front. 7 (2020) 622–627, https://doi.org/10.1039/c9qo01446b.
[4] J. Zhang, Y. Li, R. Xu, Y. Chen, Donor-acceptor complex enables alkoxyl radical generation for metal-free C(sp3)-C(sp3) cleavage and allylation/alkenylation, Angew. Chem. Int. Ed. Engl. 56 (2017) 12619–12623, https://doi.org/10.1002/anie.201707171.
[5] X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang, J.-P. Cheng, Hydride, hydrogen atom, proton, and electron transfer driving forces of various five-membered heterocyclic organic hydrides and their reaction intermediates in acetonitrile, J. Am. Chem. Soc. 130 (2008) 2501–2516, https://doi.org/10.1021/ja075523m.
[6] E. Hasegawa, S. Takizawa, Redox chemistry of benzimidazoline (BIH) and benzimidazolium (BI^+)-initiation, exploration and expansion-, J. Synth. Org. Chem., Jpn. 82 (2024) 1001–1018, https://doi.org/10.5059/yukigoseikyokaishi.82.1001.
[7] J. Cheng, K.L. Handoo, V.D. Parker, Hydride affinities of carbenium ions in acetonitrile and dimethyl sulfoxide solution, J. Am. Chem. Soc. 115 (1993) 2655–2660, https://doi.org/10.1021/ja00060a014.
[8] J. Cheng, K.L. Handoo, J. Xue, V.D. Parker, Free energy hydride affinities of quinones in dimethyl sulfoxide solution, J. Org. Chem. 58 (1993) 5050–5054, https://doi.org/10.1021/jo00071a011.
[9] X.-M. Zhang, J.W. Bruno, E. Enyinnaya, Hydride affinities of arylcarbenium ions and iminium ions in dimethyl sulfoxide and acetonitrile, J. Org. Chem. 63 (1998) 4671–4678, https://doi.org/10.1021/jo980120d.
[10] J.T. Muckerman, P. Achord, C. Creutz, D.E. Polyansky, E. Fujita, Calculation of thermodynamic hydricities and the design of hydride donors for CO2 reduction, Proc. Natl. Acad. Sci. U. S. A. 109 (2012) 15657–15662, https://doi.org/10.1073/pnas.1201026109.
[11] S. Ilic, A. Alherz, C.B. Musgrave, K.D. Glusac, Thermodynamic and kinetic hydricities of metal-free hydrides, Chem. Soc. Rev. 47 (2018) 2809–2836, https://doi.org/10.1039/C7CS00171A.
[12] S. Ilic, U. Pandey Kadel, Y. Basdogan, J.A. Keith, K.D. Glusac, Thermodynamic hydricities of biomimetic organic hydride donors, J. Am. Chem. Soc. 140 (2018) 4569–4579, https://doi.org/10.1021/jacs.7b13526.
[13] R.B. Weerasooriya, J.L. Gesiorski, A. Alherz, S. Ilic, G.N. Hargenrader, C. B. Musgrave, K.D. Glusac, Kinetics of hydride transfer from catalytic metal-free hydride donors to CO2, J. Phys. Chem. Lett. 12 (2021) 2306–2311, https://doi.org/10.1021/acs.jpclett.0c03662.
[14] S. Ilic, J.L. Gesiorski, R.B. Weerasooriya, K.D. Glusac, Biomimetic metal-free hydride donor catalysts for CO2 reduction, Acc. Chem. Res. 55 (2022) 844–856, https://doi.org/10.1021/acs.accounts.1c00708.
[15] H. Mayr, M. Patz, Scales of nucleophilicity and electrophilicity: a system for ordering polar organic and organometallic reactions, Angew. Chem., Int. Ed. Engl. 33 (1994) 938–957, https://doi.org/10.1002/anie.199409381.
[16] H. Mayr, G. Lang, A.R. Ofial, Reactions of carbocations with unsaturated hydrocarbons: electrophilic alkylation or hydride abstraction? J. Am. Chem. Soc. 124 (2002) 4076–4083, https://doi.org/10.1021/ja0121538.
[17] D. Richter, H. Mayr, Hydride-donor abilities of 1,4-dihydropyridines: a comparison with pi nucleophiles and borohydride anions, Angew. Chem. Int. Ed Engl. 48 (2009) 1958–1961, https://doi.org/10.1002/anie.200804263.
[18] D. Richter, Y. Tan, A. Antipova, X.-Q. Zhu, H. Mayr, Kinetics of hydride abstractions from 2-arylbenzimidazolines, Chem. Asian J. 4 (2009) 1824–1829, https://doi.org/10.1002/asia.200900322.
[19] E. Hasegawa, T. Ohta, S. Tsuji, K. Mori, K. Uchida, T. Miura, T. Ikoma, E. Tayama, H. Iwamoto, S.-Y. Takizawa, S. Murata, Aryl-substituted dimethylbenzimidazolines as effective reductants of photoinduced electron transfer reactions, Tetrahedron 71 (2015) 5494–5505, https://doi.org/10.1016/j.tet.2015.06.071.
[20] D. Nicewicz, H. Roth, N. Romero, Experimental and calculated electrochemical potentials of common organic molecules for applications to single-electron redox chemistry, Synlett 27 (2015) 714–723, https://doi.org/10.1055/s-0035-1561297.
[21] S. Ilic, A. Alherz, C.B. Musgrave, K.D. Glusac, Importance of proton-coupled electron transfer in cathodic regeneration of organic hydrides, Chem. Commun. (Camb.) 55 (2019) 5583–5586, https://doi.org/10.1039/c9cc00928k.
[22] R. Matsubara, T. Harada, W. Xie, T. Yabuta, J. Xu, M. Hayashi, Sensitizer-free photochemical regeneration of benzimidazoline organohydride, J. Org. Chem. 88 (2023) 12276–12288, https://doi.org/10.1021/acs.joc.3c00898.
[23] I.-S.H. Lee, H.J. Kil, Y.R. Ji, Reactivities of acridine compounds in hydride transfer reactions, J. Phys. Org. Chem. 20 (2007) 484–490, https://doi.org/10.1002/poc.1182.
[24] Y.-S. Lee, Y.-H. Cho, S. Lee, J.-K. Bin, J. Yang, G. Chae, C.-H. Cheon, Significant facilitation of metal-free aerobic oxidative cyclization of imines with water in synthesis of benzimidazoles, Tetrahedron 71 (2015) 532–538, https://doi.org/10.1016/j.tet.2014.12.043.
[25] T.-K.-C. Huynh, T.-H.-A. Nguyen, N.-H.-S. Tran, T.-D. Nguyen, T.-K.-D. Hoang, A facile and efficient synthesis of benzimidazole as potential anticancer agents, J. Chem. Sci. (Bangalore) 132 (2020) 1–9, https://doi.org/10.1007/s12039-020-01783-4.
[26] Y.-Q. Jiang, S.-H. Jia, X.-Y. Li, Y.-M. Sun, W. Li, W.-W. Zhang, G.-Q. Xu, An efficient NaHSO3-promoted protocol for chemoselective synthesis of 2-substituted benzimidazoles in water, Chem. Pap. 72 (2018) 1265–1276, https://doi.org/10.1007/s11696-017-0367-5.
[27] A.G. Wright, T. Weissbach, S. Holdcroft, Poly(phenylene) and m-terphenyl as powerful protecting groups for the preparation of stable organic hydroxides, Angew. Chem. Int. Ed Engl. 55 (2016) 4818–4821, https://doi.org/10.1002/anie.201511184.
[28] L.-L. Zhao, W. Liu, Z. Zhang, H. Zhao, Q. Wang, X. Yan, Ruthenium-catalyzed ortho- and meta-H/D exchange of arenes, Org. Lett. 21 (2019) 10023–10027, https://doi.org/10.1021/acs.orglett.9b03955.
[29] R. Iakovenko, J. Hlaváč, Visible light-mediated metal-free double bond deuteration of substituted phenylalkenes, Green Chem. 23 (2021) 440–446, https://doi.org/10.1039/d0gc03081c.
[30] N. Proust, J.C. Gallucci, L.A. Paquette, Effect of sulfonyl protecting groups on the neighboring group participation ability of sulfonamido nitrogen, J. Org. Chem. 74 (2009) 2897–2900, https://doi.org/10.1021/jo900065q.
[31] T. Vlaar, R.C. Cioc, P. Mampuys, B.U.W. Maes, R.V.A. Orru, E. Ruijter, Sustainable synthesis of diverse privileged heterocycles by palladium-catalyzed aerobic oxidative isocyanide insertion, Angew. Chem. Int. Ed Engl. 51 (2012) 13058–13061, https://doi.org/10.1002/anie.201207410.

[32] P. Brunet, J.D. Wuest, Formal transfers of hydride from carbon–hydrogen bonds. Attempted generation of H2 by intramolecular protonolyses of the activated carbon–hydrogen bonds of dihydrobenzimidazoles, Can. J. Chem. 74 (1996) 689–696, https://doi.org/10.1139/v96-074.

[33] E. Hasegawa, N. Izumiya, T. Miura, T. Ikoma, H. Iwamoto, S.-Y. Takizawa, S. Murata, Benzimidazolium naphthoxide betaine is a visible light promoted organic photoredox catalyst, J. Org. Chem. 83 (2018) 3921–3927, https://doi.org/10.1021/acs.joc.8b00282.

[34] S. Riera-Galindo, A. Orbelli Biroli, A. Forni, Y. Puttisong, F. Tessore, M. Pizzotti, E. Pavlopoulou, E. Solano, S. Wang, G. Wang, T.-P. Ruoko, W.M. Chen, M. Kemerink, M. Berggren, G. di Carlo, S. Fabiano, Impact of singly occupied molecular orbital energy on the n-doping efficiency of benzimidazole derivatives, ACS Appl. Mater. Interfaces 11 (2019) 37981–37990, https://doi.org/10.1021/acsami.9b12441.

[35] I.-S.H. Lee, E.H. Jeoung, M.M. Kreevoy, Marcus theory of a parallel effect on α for hydride transfer reaction between NAD+ analogues, J. Am. Chem. Soc. 119 (1997) 2722–2728, https://doi.org/10.1021/ja963768l.

[36] R. Miyajima, T. Kiuchi, Y. Ooe, H. Iwamoto, S.-Y. Takizawa, E. Hasegawa, Electron and hydrogen atom donor photocatalysts in situ generated from benzimidazolium salts and hydride reagents, J. Photochem. Photobiol., A 16 (2023) 100195, https://doi.org/10.1016/j.jpap.2023.100195.

[37] H. Chikashita, H. Ide, K. Itoh, 1,3-Dimethyl-2-phenylbenzimidazoline as a novel and efficient reagent for mild reductive dehalogenation of .alpha.-halo carbonyl compounds and acid chlorides, J. Org. Chem. 51 (1986) 5400–5405, https://doi.org/10.1021/jo00376a064.

[38] J. Chen, D.D. Tanner, New method for the facile reduction of .alpha.-nitro sulfones to nitroalkanes via an electron-transfer-hydrogen atom abstraction mechanism, J. Org. Chem. 53 (1988) 3897–3900, https://doi.org/10.1021/jo00252a001.

[39] E. Hasegawa, T. Kato, T. Kitazume, K. Yanagi, K. Hasegawa, T. Horaguchi, Photoinduced electron transfer reactions of α,β-epoxy ketones with 2-phenyl-N,N-dimethylbenzimidazoline (PDMBI): significant water effect on the reaction pathway, Tetrahedron Lett. 37 (1996) 7079–7082, https://doi.org/10.1016/0040-4039(96)01578-x.

[40] Y. Tamaki, K. Koike, T. Morimoto, O. Ishitani, Substantial improvement in the efficiency and durability of a photocatalyst for carbon dioxide reduction using a benzoimidazole derivative as an electron donor, J. Catal. 304 (2013) 22–28, https://doi.org/10.1016/j.jcat.2013.04.002.

[41] Y. Tamaki, T. Morimoto, K. Koike, O. Ishitani, Photocatalytic CO2 reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes, Proc. Natl. Acad. Sci. U. S. A. 109 (2012) 15673–15678, https://doi.org/10.1073/pnas.1118336109.

[42] C.-H. Lim, S. Ilic, A. Alherz, B.T. Worrell, S.S. Bacon, J.T. Hynes, K.D. Glusac, C. B. Musgrave, Benzimidazoles as metal-free and recyclable hydrides for CO2 reduction to formate, J. Am. Chem. Soc. 141 (2019) 272–280, https://doi.org/10.1021/jacs.8b09653.

[43] S. Rohrbach, R.S. Shah, T. Tuttle, J.A. Murphy, Neutral organic super electron donors made catalytic, Angew. Chem. Int. Ed Engl. 58 (2019) 11454–11458, https://doi.org/10.1002/anie.201905814.

[44] E. Hasegawa, T. Tanaka, N. Izumiya, T. Kiuchi, Y. Ooe, H. Iwamoto, S.-Y. Takizawa, S. Murata, Protocol for visible-light-promoted desulfonylation reactions utilizing catalytic benzimidazolium aryloxide betaines and stoichiometric hydride donor reagents, J. Org. Chem. 85 (2020) 4344–4353, https://doi.org/10.1021/acs.joc.0c00038.

[45] R. Miyajima, M. Okamura, K. Oomori, H. Iwamoto, K. Wakamatsu, E. Hasegawa, Desulfonylative radical truce–smiles rearrangement utilizing the benzimidazoline and benzimidazolium redox couple, Synlett 35 (2024) 352–356, https://doi.org/10.1055/a-2153-6594.

[46] T. Kawawaki, Y. Akinaga, D. Yazaki, H. Kameko, D. Hirayama, Y. Negishi, Promoting photocatalytic carbon dioxide reduction by tuning the properties of cocatalysts, Chemistry 29 (2023) e202203387, https://doi.org/10.1002/chem.202203387.

[47] R.B. Weerasooriya, M.C. Drummer, B.T. Phelan, J.L. Gesiorski, E.A. Sprague-Klein, L.X. Chen, K.D. Glusac, Toward metal-free photocatalysis: photochemical regeneration of organic hydride donors using phenazine-based photosensitizers, J. Phys. Chem. C Nanomater. Interfaces 126 (2022) 17816–17825, https://doi.org/10.1021/acs.jpcc.2c03541.

[48] W. Xie, J. Xu, U. Md Idros, J. Katsuhira, M. Fuki, M. Hayashi, M. Yamanaka, Y. Kobori, R. Matsubara, Metal-free reduction of CO2 to formate using a photochemical organohydride-catalyst recycling strategy, Nat. Chem. 15 (2023) 794–802, https://doi.org/10.1038/s41557-023-01157-6.