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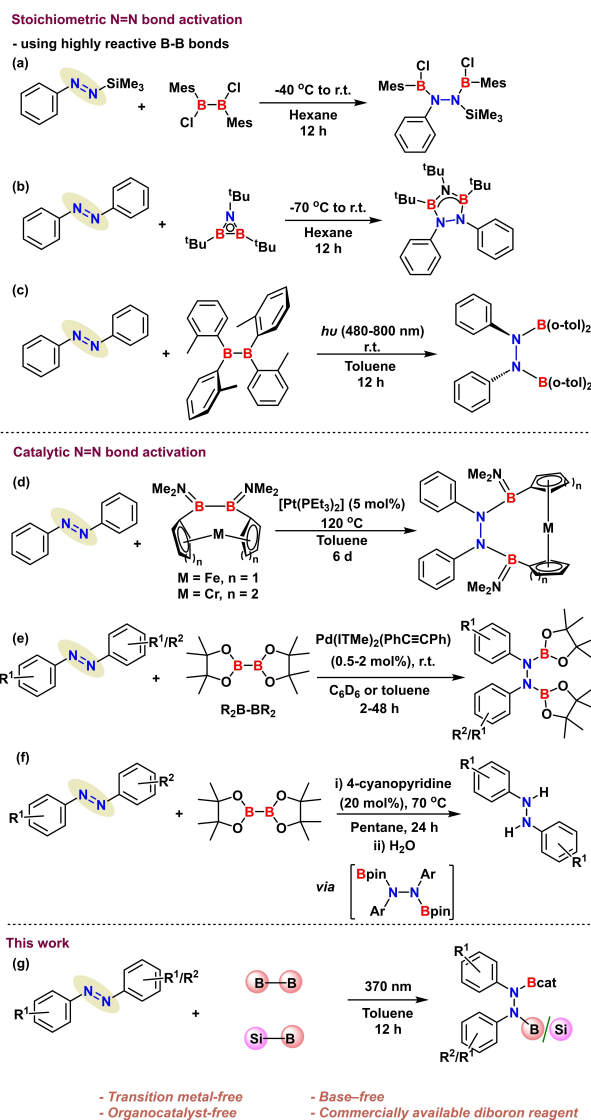www.angewandte.org

Main-Group Chemistry

Catalyst-Free Diborylation and Silaboration of Azoarenes: A Simple Photoinduced Approach

Reetu Rani Mondal, Apurba Kumar Pal, and K. Geetharani*

Abstract: The diborylation of the N=N double bond of azoarenes has been achieved using a commercially available diboron reagent, B_2cat_2 [bis(catecholato)diboron]. By utilizing the photo-switchable nature of azoarenes under blue-LED light irradiation, an uncatalyzed diborylation and silaboration yielded a broad range of functionalized hydrazine derivatives. The mechanistic origin validates the importance of *cis* configuration, which is corroborated by theoretical calculations.

The Lewis acidic diboron compounds often display an interesting reactivity and have witnessed significant interest because of the unusual reactivity of these compounds.[1] The highly Lewis acidic diboron tetrahalides B_2X_4 readily undergoes uncatalyzed addition across the C=C and C≡C bonds, leading to a complex product.[2] In contrast, the more electron-rich and less Lewis-acidic tetraalkoxydiborane(4) compounds $B_2(OR)_4$, in general, require the presence of a transition metal catalyst for such additions across the unsaturated carbon-carbon bonds.[3] In recent advances, an interesting chemistry has been developed for the activation of more stable diboron compounds $B_2(OR)_4$ by the Lewis bases via anionic sp^2–sp^3 diborane adducts or by solvent coordination.[4] In literature, there are numerous reports on the diborylation of unsaturated compounds like alkenes, alkynes, α, β-unsaturated compounds, etc., to yield their corresponding boronic esters in the absence of transition metals.[5] However, similar reactions other than carbon-based unsaturated compounds are restricted to a few. The diboration of N=N double bonds in azo compounds has rarely been explored in the presence or absence of a catalyst. Only highly reactive diboron compounds such as dimesityldiboron dichloride, R(Cl)B-B(Cl)R (R=Mes),[6] and azadiboriridine $NB_2{}^tBu_3$,[7] were used to achieve the diboration of the diazene to yield the *N, N′*-diborylated hydrazine (Scheme 1a–b). The potential applicability of these methods was limited due to the arduous synthesis of the diboron reagent employed. The other way of diboration of the N=N double bond of azobenzene was by the highly strained [2]borametalloarenophanes (Scheme 1d).[8] Later,
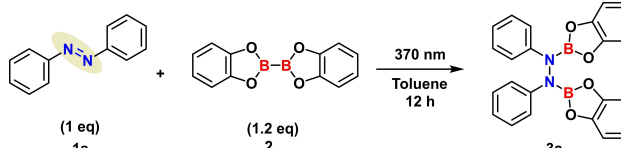
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Scheme 1. Previous works on diborylation of N=N double bonds (**a–f**). Catalyst-free photoinduced diborylation and silaboration of azoarenes (**g**).

the collaborative work by Braunschweig, Navarro and Spencer reported diborylation and the first-ever report on the silaboration of azoarenes using a transition metal-based catalyst, [Pd(ITMe)₂(PhC≡CPh)] and B_2pin_2 (Scheme 1e).[9] After the development of diborane adduct with the Lewis base/solvents, Li and co-workers have demonstrated the catalytic reduction of the N=N double bond of azoarenes

using a commercially available diboron reagent, bis(pinacolato)diboron via the generation of a captodatively-stabilized boryl radical by using 4-cyanopyridine as the organocatalyst (Scheme 1f).[10] In 2019, a highly Lewis-acidic tetraaryldiborane (o-tol)₂B-B(o-tol)₂ was synthesized from B₂cat₂ and showed uncatalyzed diborylation of azobenzene under visible-light irradiation (Scheme 1c).[11] In all these metal-free activations, the Lewis acidity of diboron compounds plays a major role in determining the substrate's reactivity. Later, Song et al., achieved the transfer hydrogenation of azobenzenes to hydrazobenzenes via the diborylation in the presence of MeOH.[12]

It is well known that the azo-based compounds have been used as photoswitches because of their interesting property of swapping between the two isomeric forms on irradiation of light with different wavelengths.[13] Azoarenes are stable in their *trans*-orientation and attain their *cis*-form on exposure to UV light and can come back to their stable conformation in the presence of visible light or under thermal conditions.[14] Based on our previous studies on metal-free diboron activation,[15] we envisaged that the *cis*-conformer of azoarenes may help in the cleavage of commercially available and highly Lewis acidic B₂cat₂ (cat = 1,2-O₂C₆H₄) for the synthesis of bis(boryl)hydrazines under suitable wavelength irradiation. Herein, we demonstrate a simple metal and additive-free protocol for both diboration and silaboration of the N=N double bond of azoarenes under blue-LED conditions (Scheme 1g). Noteworthy that the catalyst-free silaboration of azobenzene is unknown.[9]

We commenced the reaction by choosing (*E*)-1,2-diphenyldiazene, **1a** and B₂cat₂ in benzene under 370 nm blue-LED light, as the azo compounds are known to attain *cis*-geometry under UV light conditions. To our delight, we obtained a peak at 26.7 ppm in ¹¹B NMR, indicating the formation of a tricoordinate B–N bonded compound.[9,15–16] It was consistent with the diboration of substituted azoarenes achieved using a Pd-catalyst.[9] The reaction was further optimized using **1a** as the model substrate. First, the equivalence of the diboron reagent was screened for the reductive diboration reaction; the reaction of azobenzene with 1.2 equivalent of B₂cat₂ under 370 nm light irradiation for 12 h using toluene as the solvent gave 93% of diborylated product (entry 1 in Table 1). The formation of the **3a** was reduced with the use of 1 equivalent of B₂cat₂, employing more amounts did not improve the yield (entries 2–3 in Table 1). Other diboron reagents, bis(pinacolato)diboron, B₂pin₂, bis(neopentyl glycolato)diboron, B₂neop₂ and B₂pai₂ gave no product or trace amount of product (entries 4–6) under the reaction conditions. This behavior clearly indicates that Lewis acidic diboron reagent is crucial for the N=N double bond activation as B₂cat₂ is more Lewis acidic than B₂pin₂, B₂neop₂ and B₂pai₂.[1a,17] Further, solvents were screened for the reaction; the polar solvents, such as dimethylacetamide and dimethylformamide, gave no product (entries 7 and 8). Dioxane and THF yielded 48% and 15% of the product, respectively (entries 9–10). Hexane was found to be inferior under the reaction conditions (entry 11). Changing the solvent to benzene yielded 88% product (entry 12). Control
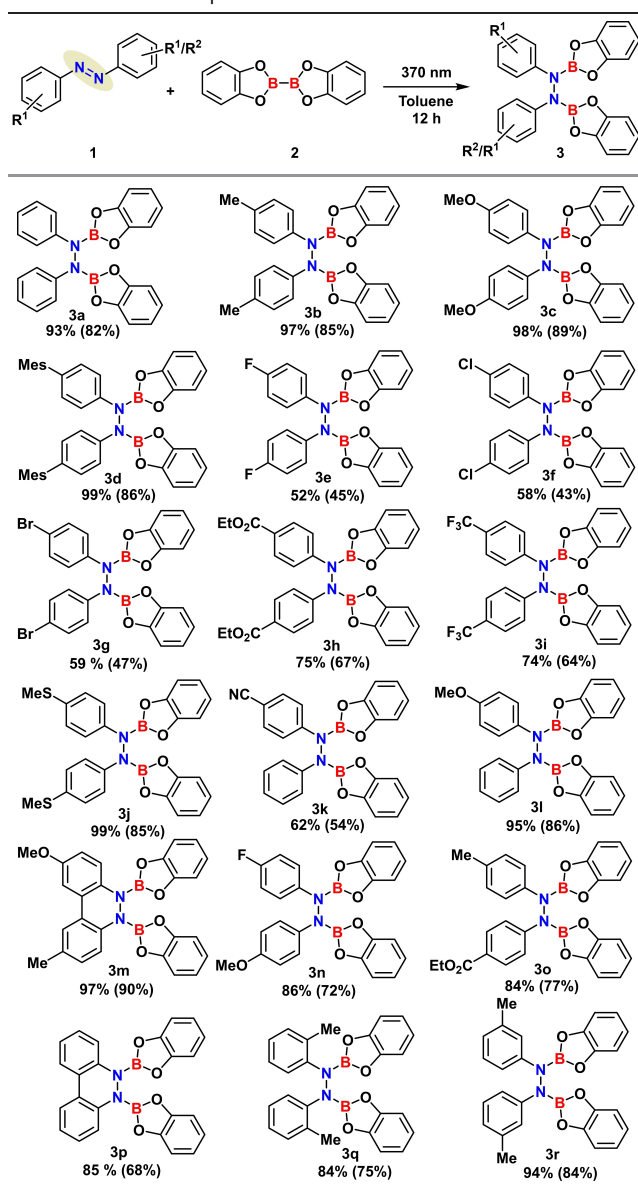
Table 1: Optimization of reaction conditions.[a]

Entry	Variation from standard reaction conditions	Yield[b] (%)
1	none	93
2	1 eq. of B₂cat₂	76
3	1.5 eq. of B₂cat₂	92
4	B₂pin₂ instead of B₂cat₂	n.d.[c]
5	B₂neop₂ instead of B₂cat₂	trace
6	B₂pai₂ instead of B₂cat₂	n.d.[c]
7	DMAc instead of toluene	n.d.[c]
8	DMF instead of toluene	n.d.[c]
9	Dioxane instead of toluene	48
10	THF instead of toluene	15
11	Hexane instead of toluene	26
12	Benzene instead of toluene	88
13	without light	n.d.[c]
14	9 h instead of 12 h	80
15	24 h instead of 12 h	93

[a]Standard reaction conditions: Compound **1a** (0.1 mmol), B₂cat₂ (0.12 mmol), in toluene (0.5 ml) under N₂, rt, 12 h, 40 W blue Kessil LED lamp. [b]Yields were determined by ¹H nuclear magnetic resonance (NMR) analysis using tetraethylsilane as the internal standard. [c] not determined.

experiments showed that light plays a key role in the reaction, as without any light source, the reaction did not proceed (entry 13). This suggested that the *cis* isomer is taking part in the reaction. The necessity of light was also confirmed by conducting light on/off experiment (Figure S2). Reducing the reaction time to 9 h gave 80% yield (entry 14). Increasing the reaction time to 24 h did not improve the yield (entry 15, see Supporting Information Section III).

With the optimized reaction conditions in hand, we started exploring the substrate scope for the reductive diborylation reaction of azoarenes (Table 2). The ¹H NMR yield, along with the isolated yield for the 1,2-bis-(boryl)hydrazine derivatives (**3a–3r**) of various substituted diazenes, are shown in Table 2. Different functional-group-bearing azoarenes were synthesized according to reported procedures (see Supporting Information). Compound **3a** was isolated in 82% yield after multiple precipitations using THF/hexane. Colorless crystals of **3a** were obtained from toluene at −30 °C. Single-crystal X-ray diffraction analysis further confirmed the formation of the diborylated compound (Figure 1). The molecular structure is similar to the one obtained using B₂pin₂ and Pd-NHC catalyst.[9] The N–N bond length of 1.423(2) Å is much longer than the N=N double of azobenzene, 1.25 Å,[18] and is similar to the bond lengths of reported diphenyl hydrazines, 1.394(7) Å.[19] Both the nitrogen atoms are in distorted trigonal planar geometry [113.4(1)–130.6(2)°; N1, N2: Σ = 360°]. The boron atoms B1 and B2 also exhibit distorted trigonal planar geometry [112.5(2)–127.0(2)°; B1, B2: Σ = 360°]. The B–N bond lengths of 1.422(3) and 1.414(3) Å are comparable to that of the

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Table 2: Substrate scope for the diboration of azoarenes.[a,b,c]

3a 93% (82%)
3b 97% (85%)
3c 98% (89%)
3d 99% (86%)
3e 52% (45%)
3f 58% (43%)
3g 59% (47%)
3h 75% (67%)
3i 74% (64%)
3j 99% (85%)
3k 62% (54%)
3l 95% (86%)
3m 97% (90%)
3n 86% (72%)
3o 84% (77%)
3p 85% (68%)
3q 84% (75%)
3r 94% (84%)

[a]Reaction conditions: Compound 1a (0.1 mmol), B₂cat₂ (0.12 mmol) in toluene (0.5 ml) under N₂, rt, 12 h, 40 W blue Kessil LED lamp. [b]Yields were determined by ¹H nuclear magnetic resonance (NMR) analysis using tetraethylsilane as the internal standard. [c]Isolated yields are given in brackets for 0.3 mmol scale reaction.

reported aminoboranes.[9] The reaction gave excellent yield with symmetrical electron-donating substituents in the para position of the benzene ring.

The methyl-**1b**, methoxy-**1c**, and mesityl- **1d**, substituted ones gave excellent yields of 97%, 98% and 99% respectively. However, using the electron-withdrawing-substituents, fluoro-, chloro-, bromo-, ethoxycarbonyl- and trifluoromethyl- (**1e**–**1i**), a moderate to good yield of the product was obtained. Thiomethyl group was well tolerated under the standard reaction conditions (**1j**). Diazo compounds with unsymmetrical substitution on the benzene rings (**1k**–**1l**), also furnished the product with good to
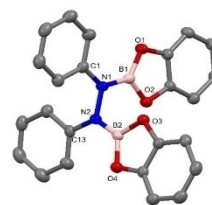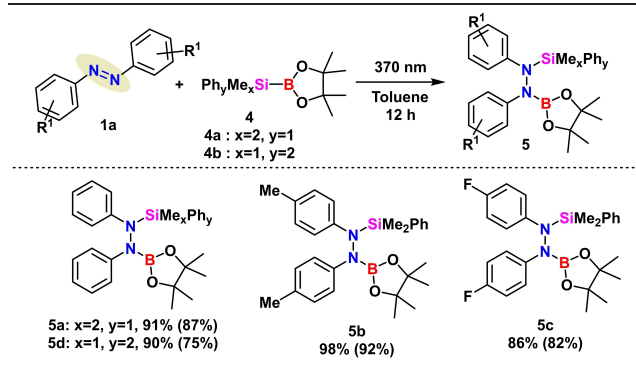

Figure 1. Molecular structure of **3a** with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–N2: 1.423(2), N1–B1: 1.422(3), N2–B2: 1.414(3), C1–N1–B1: 130.6(2), N2–N1–B1: 113.4(1), N2–N1–C1: 115.7(1), C13–N2–B2: 129.2(2), N1–N2–B2: 114.6(1), N1–N2–C13: 116.2(1), O1–B1–C2: 112.7(2), O1–B1–N1: 127.0(2), O2–B1–N1: 120.3(2), O4–B2–O3: 112.5(2), O4–B2–N2: 126.0(2), O3–B2–N2: 121.5(2).

excellent yield. Azoarene with two different electron-donating groups gave 97% of product (**1m**). Substrates with the electron-withdrawing group on one benzene ring and an electron-donating group on the other ring were also well tolerated (**1n**, **1o**). The reaction using aromatic benzo-[c]-cinnoline (**1p**) gave a good yield of 85% under the optimized reaction conditions. The ortho- and meta-substituted diazenes also gave very good yields of 84% and 94%, respectively (**1q**, **1r**). The aliphatic azo compounds were found not suitable for this reaction (see Supporting Information).

Since our standard reaction conditions were suitable to activate the B–B bond of B₂(OR)₄, which has high bond-dissociation energy, the scope of the photo-mediated reaction was further extended for the silaboration of azoarenes. When 1 equivalent of (E)-1,2-diphenyldiazene was reacted with 1.2 equivalents of (dimethylphenyl)silylboronic acid pinacol ester PhMe₂Si-Bpin, the ¹¹B NMR spectra showed a peak at 25.4 ppm, indicating the cleavage of B–Si bond of silaborane and the formation of a tricoordinate B–N compound **5a**. The reaction was carried out using electron-donating and electron-withdrawing group-containing azoarenes **1b** and **1e**, which gave excellent yields, showing the versatility of the protocol (Table 3). The reaction of **1a** with methyldiphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) silane, Ph₂MeSi-Bpin also proceeded well to give the corresponding silaborated product **5d**. Slow evaporation of a toluene solution of **5b** gave colourless crystals suitable for X-ray analysis (Figure 2). The crystal structure was solved in the P2₁/c space group; the N1–N2 bond length of 1.431(4) Å is comparable to that of **3a** and is similar to the reported silyl substituted hydrazines.[20] The Si1–N1 bond length of 1.762(3) Å is slightly longer than the bond reported for silyl amines of form R₃SiNR'₂; however, it is smaller than the one reported by Braunschweig, Navarro and Spencer.[21,9] The N2-B1 bond length of 1.430(6) Å resembles **3a** and is comparable to the other aminoboranes. Both the nitrogen atoms are present in distorted trigonal planar geometry [115.0(3)–129.2(3)°; N1, N2: Σ=360°]. The boron B1 also exhibits distorted trigonal planar geometry [113.9(4)–125.0(4)°; B1: Σ=360°] as in the diborylated product. When **3a** was treated with degassed, deionized H₂O, 1,2-diphenylhy-

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Table 3: Substrate scope for the silaboration of azoarenes.[a,b,c]

[a]Standard reaction conditions: Compound **1a** (0.1 mmol), R₃Si-Bpin (0.12 mmol), 40 W blue Kessil LED lamp in toluene (0.5 ml) under N₂, rt, 12 h. [b]Yields were determined by ¹H nuclear magnetic resonance (NMR) analysis using tetraethylsilane as the internal standard. [c]Isolated yields are given in brackets for 0.3 mmol scale reaction.
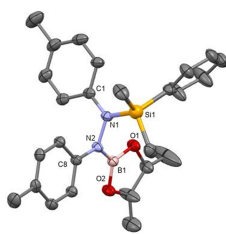

Figure 2. Molecular structure of **5b** with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–N2: 1.431(4), N1–Si1: 1.762(3), N2–B1: 1.430(6), C1–N1–Si1: 127.8(3), N2–N1–Si1: 116.3(3), N2–N1–C1: 115.4(3), C8–N2–B1: 129.2(3), N1–N2–B1: 115.0(3), N1–N2–C8: 115.6(3), O1–B1–N2: 121.2(4), O1–B1–O2: 113.9(4), O2–B1–N2: 125.0(4).

drazine **6** was produced in an isolated yield of 86%, demonstrating the synthetic usefulness of the 1,2-(bisboryl)diazene compounds. Furthermore, **3a** can also be converted to N, N′-diphenylpivalohydrazide **7** by reacting it with pivaloyl chloride (Scheme 2).

To obtain mechanistic insight, the reaction of **1a** and B₂cat₂ was performed under standard conditions in the presence of radical scavengers, 9,10-dihydroanthracene (DHA) and 1,1-diphenylethylene (1,1-DPE); no observable impact on the yield (Scheme 3a) was noticed. Further, an experiment was conducted with **1a** and equimolar amounts of B₂cat₂ and 2,2′-bibenzo[d][1,3,2]dithiaborole, B₂(dithiocat)₂ under optimized reaction conditions; no cross-
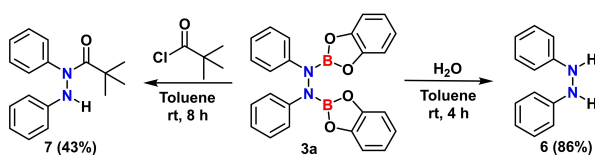
Scheme 2. Synthetic utility of 1,2-bis(boryl)hydrazines
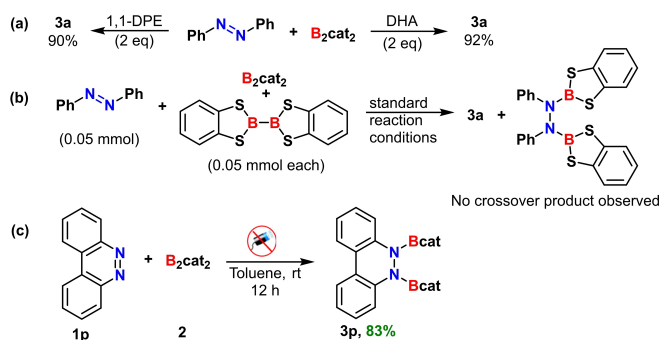
Scheme 3. (a) Diborylation reaction in the presence of radical scavengers: 9,10-dihydroanthracene (DHA) and 1,1-diphenylethylene (1,1-DPE) (b) crossover experiment (c) diborylation under dark condition.

over product was observed (Scheme 3b). These experiments confirmed that radical is not involved in the reaction.

Further, to establish the role of the *cis* isomer in the reaction, benzo[c]cinnoline, **1p** was chosen as a substrate, as it exists in *cis* orientation at ambient conditions (Scheme 3c). We also envisaged that if the role of the light source is only to convert *trans* into *cis* form, the reaction of **1p** with **2** must yield the product **3p** under dark conditions. As expected, a similar yield of the diborylated product was obtained without any light. This study confirmed 1) the necessity of the *cis* configuration to facilitate product formation and 2) for other diazenes, the UV light helps to convert the stable *trans*-conformer to its *cis* form, which actively participates in the reaction.

The next investigation was on the possible reaction pathway, DFT calculations were carried out using the B3LYP method and 6-31+G basis set, which supported stepwise coordination over a concerted pathway (Scheme 4a). On irradiating with light, **1a** attains the *cis* orientation, and **1a'+2** can undergo two possible pathways: i) concerted and ii) stepwise coordination. The **TS1** and **TS2** for the stepwise pathway are more stabilized than **TS-conc** for the concerted mechanism. This observation is consistent with the stepwise coordination proposed by Katsuma et al.[11] To get experimental evidence of the intermediate species in the reaction, ¹¹B NMR was recorded after 30 mins. A chemical shift of 8.4 ppm was observed, which disappeared after 12 h, indicating the formation of a tetracoordinate intermediate during the reaction.[22]

Based on the experimental observations, DFT studies and previous reports,[11] a plausible mechanism for the reduction of azoarenes to 1,2-bis(boryl)hydrazines has been proposed (Scheme 4b). Initially, *trans* azoarenes (**1a–r**) attain their respective *cis* conformation on irradiation with 370 nm UV light. **1a'–r'** then reacts with Lewis-acidic B₂cat₂ via the coordination of a nitrogen with a boron to form **Int A**. Further, the other Bcat unit migrates to the non-coordinated nitrogen of **Int A** to give the diborylated product **3a–r**.

In conclusion, we have demonstrated that azoarenes' photoswitchability can be used to facilitate their diborylation into 1,2-bis(boryl)hydrazines in the absence of a catalyst or
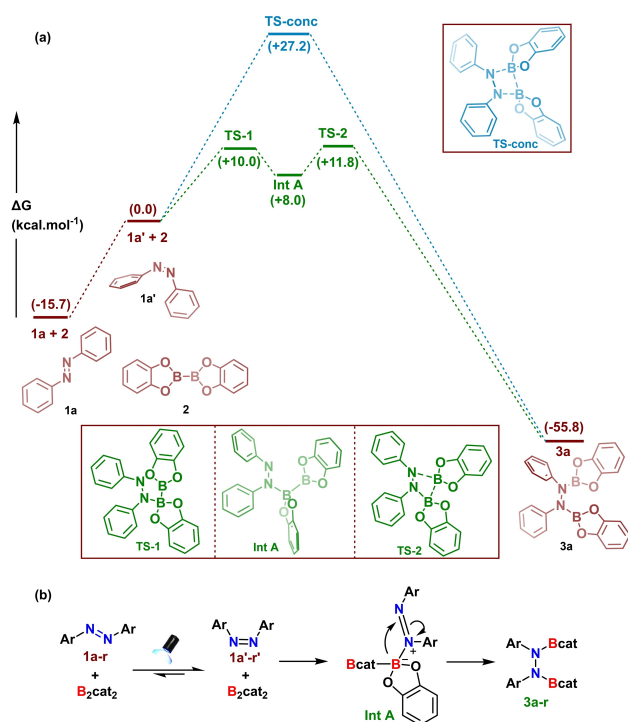
Scheme 4. (a) DFT calculations (b) Possible mechanism.

a base. The developed protocol is simple and uses a commercially available diboron reagent B_2cat_2 under very mild reaction conditions. The versatility of the reaction is shown by using various functional group substituents on the phenyl ring. Mechanistic investigations excluded the involvement of a radical pathway and suggested a stepwise coordination mechanism for the transformation. Furthermore, this procedure was expanded to produce 1-silyl-2-borylhydrazines by activating silaboranes. To the best of our knowledge, this is the first report on metal-free silaboration of azoarenes. Moreover, 1,2-bis(boryl)hydrazines can be transformed into hydrazines, and N-acylhydrazides, which can be useful in organic synthesis. More such transformations based on photoswitchability of azo compounds are underway in our laboratory.

Supporting Information

Experimental details and characterization data. Additional references cited within the Supporting Information.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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[23] Deposition numbers CCDC 2377876 (for **3a**) and CCDC 2377878 (for **5b**), contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Communication

Main-Group Chemistry

R. R. Mondal, A. K. Pal,
K. Geetharani* —————— **e202415913**

Catalyst-Free Diborylation and Silaboration
of Azoarenes: A Simple Photoinduced Ap-
proach
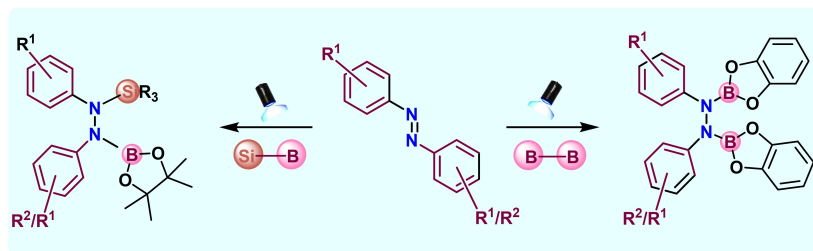
- *Transition metal-free*   - *Wide substrate scope*   - *Base–free*
- *Organocatalyst-free*   - *Mild reaction conditions*   - *Commercially available diboron reagent*

We have shown that, in the absence of a catalyst or a base, azoarenes' photo-switchability can be exploited to aid in their diborylation into 1,2-bis-(boryl)hydrazines. The transformation is achieved using commercially available diboron reagent, bis(catecholato)diboron and extremely mild conditions are used in the devised approach. Moreover, silaboranes were also activated using this process to yield 1-silyl-2-borylhydrazines.