Project Completion Report

1.	DST reference No.	**INT/FRG/DAAD/P-9/2016**
2.	Project title	**Homocoupling, Heterocoupling and Liberation of Borylene Ligands**
3.	Objectives	**(A) Understanding the coupling and liberation of borylene ligands** ★ What are the mechanisms of the partial and full borylene liberation reactions? ★ Why does the boron ligand stay bound to the metal sometimes and not others? ★ What reagents or conditions would be required to ensure selective liberation of single-boron units, catenated tetraboron chains, or boron-only polymers? ★ What would the properties and stability of such liberated compounds be? **(B) Exploring the properties and reactivity of monovalent boron compounds** ★ Can we exchange the Lewis bases on the boron center as is common for metals? ★ What would be the properties of these alternative base derivatives? ★ Can photolytic CO liberation be used as a source of isolable dicoordinate boron(I)? ★ Can such a boron(I) compound perform other challenging bond activation reactions (e.g. intermolecular C-H activation), bind other Lewis bases (e.g. N_2), or even catalysis?
4.	Field of S&T covered under the project	Chemistry
5.	Project participants	
	Indian side	Foreign side
	1. Prof. Ashwini K. Phukan 2. Mr. Bitupon Borthakur, M. Sc. 3. Miss Priyam Bharadwaz, M. Sc.	1. Dr. Rian D. Dewhurst 2. Dr. Ivo Krummenacher 3. Mr. Marco Nutz, M. Sc. 4. Miss Anna Rempel
6.	Date of start of the project	01-06-2016
	Date of completion	31-05-2018

7	Visits undertaken (please include the number and duration of respective visits)		
		Name & Address of the visiting scientist	Duration of the visit
	India to Germany	1. Prof. Ashwini K. Phukan Department of Chemical Sciences, Tezpur University, Napam – 784028, Assam 2. Bitupon Borthakur Department of Chemical Sciences, Tezpur University, Napam – 784028, Assam 3. Prof. Ashwini K. Phukan Department of Chemical Sciences, Tezpur University, Napam – 784028, Assam 4. Priyam Bharadwaz Department of Chemical Sciences, Tezpur University, Napam – 784028, Assam	10.10.2016 to 30.10.2016 (21 days) 01.02.2017 to 28.02.2017 (28 days) 01.11.2017 to 25.11.2017 (25 days) 01.11.2017 to 25.11.2017 (25 days)
	Germany to India	1. Dr. Rian D. Dewhurst Institute of Inorganic Chemistry Lehrstuhl II, Am Hubland, Julius- Maximilians-Universität Würzburg, 97074 Würzburg, Germany 2. Marco Nutz Institute of Inorganic Chemistry Lehrstuhl II, Am Hubland, Julius- Maximilians-Universität Würzburg, 97074 Würzburg, Germany 3. Dr. Ivo Krummenacher Institute of Inorganic Chemistry Lehrstuhl II, Am Hubland, Julius- Maximilians-Universität Würzburg, 97074 Würzburg, Germany 4. Anna Rempel Institute of Inorganic Chemistry Lehrstuhl II, Am Hubland, Julius- Maximilians-Universität Würzburg, 97074 Würzburg, Germany	21.11.2016 to 06.12.2016 (14 days) 21.11.2016 to 06.12.2016 (14 days) 02.12.2017 to 12.12.2017 (10 days) 02.12.2017 to 12.12.2017 (10 days)

8. Yearly Project milestones

First Year (i) Isolation of intermediates in borylene liberation and theoretical calculations on the mechanism of liberation. (ii) Theoretical studies toward understanding the possibility of ligand exchange at boron and experimental attempts to realize such an exchange at boron. Second Year (i) Experimental work on liberation of boron chains and polymers and theoretical calculations towards understanding their electronic structure and stability. (ii) Experimental studies on catalysis and bond activation and theoretical calculations toward understanding the mechanism of such reactions.

9. Progress of the Project:

Accomplishment Status : (vis-à-vis the project objectives and milestones, highlighting the major/salient achievements): (Up-to 1 page)	Please see **Annexure I**
List of joint research publications (Please attach copies)	1. *Angew. Chem. Int. Ed.* **2017**, *56*, 7975. 2. *Chem. Eur. J.* **2018**, *24*, 6843.
Technology/ New Processes/ Patents generated	Not applicable as this project is fundamental in nature.
Scope for commercializing the new Scientific Knowledge	Since this project is based primarily on fundamental research, thus the discoveries made herein are unlikely to directly find practical or industrial use

10. Please elaborate with your remarks on the collaboration:

Specific advantages derived:

- Expertise
- Equipment & computational Facilities
- Exchange of Data/Samples
- Exposure to advanced technologies
- Opportunity for new interactions with any other research Organizations
- Participation in Conferences

This collaboration helped us to understand the expectations of an experimental group from their theory counterparts. We could use the state-of-the-art computational facilities that is available with Prof. Braunschweig's research group. We were also shown how sensitive experiments are being performed inside a Glove Box.

11. Application potential (immediate/long term)-

Since this project is based primarily on fundamental research, thus the discoveries made herein are unlikely to directly find practical or industrial use. However, any polymer or catalytic reaction discovered during this work may in the future find practical use after a period of development.

12. Financial details of the project-

Total project cost	Rs. 10,15,000/-
Money received	Rs. 7,53,793/- (this includes an amount of Rs. 12,209/- that was earned as bank interest)
Expenditure incurred	Rs. 5,74,952/-
Final SE/UC (in prescribed format attached	Yes

13. Conclusion summarizing the achievements and indication of scope for future work-

This highly successful collaborative research work involved experimental and theoretical work in the following areas as described in our original proposal:

(**A**) Understanding the coupling and liberation of borylene ligands and

(**B**) Exploring the properties and reactivity of monovalent boron compounds.

Subproject **A** was furthered on the German side by experimentally expanding the range of borylene complexes available and then testing these complexes with new Lewis base reagents, namely isocyanides, phosphines and CO. On the Indian side, we performed extensive calculations determining the energetic preferences for these reactions as well as their mechanisms. This work has recently led to the publication of an full paper in the high-impact general chemistry journal Chemistry - A European Journal (Release of Isonitrile- and NHC-stabilized Borylenes from Group VI Terminal Borylene Complexes, *Chem. Eur. J.* **2018**, *24*, 6843-6847).

In Subproject **B**, research on the German side included testing the heterocoupling reactivity of bulky borylene species with reagents such as azides and carbodiimides, leading to two new forms of boron-containing heterocycles, in addition to the first observations of the synthesis of a compound with a BN triple bond by using borylene complexes. On the Indian side, we performed energetic and mechanism calculations leading to the publication of a communication in the premier general chemistry journal Angewandte Chemie, International Edition (Synthesis and Trapping of Iminoboranes via M=B/C=N Bond Metathesis, *Angew. Chem. Int. Ed.* **2017**, *56*, 7975–7979).

Annexure I (Accomplishment Status)

In our first work, we have computationally {M062X/Def2-SVP, Def2-TZVP (Cr)} investigated the formation of iminoborane **2** from the reaction between **1** and diisopropylcarbodiimide (DIC) as shown below in Figure 1:

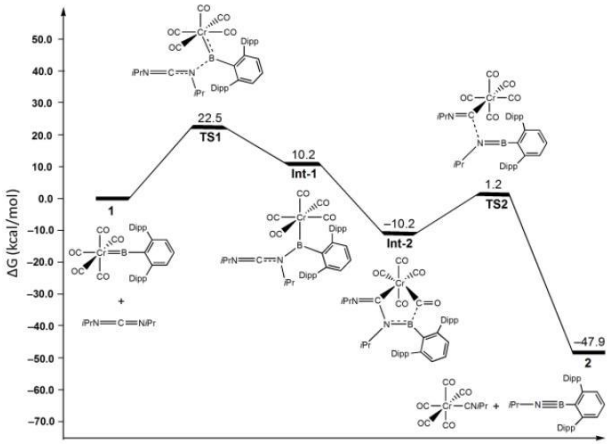

Figure 1: Proposed mechanism for the formation of **2** from **1**.

Our calculations show that the formation of **2** is overall a highly exergonic process (-47.9 kcal mol^{-1}). The formation of the first intermediate (**Int-1**) involves a transition state (**TS1**) with an activation barrier of 22.5 kcalmol^{-1}. This is followed by the coordination of the carbon atom of DIC to the chromium center, leading to the formation of the second intermediate (**Int-2**). The formation of **Int-2** from **Int-1** is an exergonic process (-20.4 kcalmol^{-1}) and can be expected to have a very shallow activation barrier, as reported in an earlier study. The final step is the most exergonic one (-37.7 kcal mol^{-1}) and corresponds to liberation of the iminoborane from **Int-2** *via* a transition state (**TS2**) with an energy barrier of 11.4 kcal mol^{-1}. The calculations show that all of the steps are exergonic except for the first nucleophilic attack by the nitrogen lone pair of DIC at the boron center, which agrees well with the requirement of elevated temperatures for the isolation of **2**.

This work has been published in *Angewandte Chemie* (*Angew. Chem. Int. Ed.* **2017**, *56*, 7975-7979).

In our second work, we have studied the reaction mechanism which involves all the possible transition states for liberation of free borylenes (**3e** and **5**) from terminal metal borylene complex [$Cr(CO)_5$(B(2,6-diphenylphenyl))] as shown below in Figure 2:

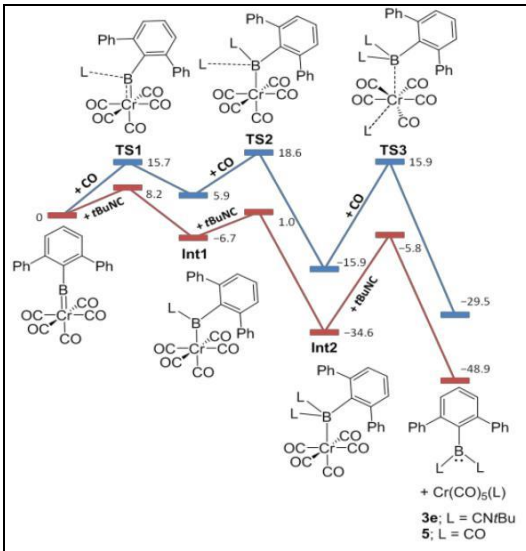

Figure 2: Proposed mechanism for liberation of **3e** and **5**. (*Chem. Eur. J*. **2018**, *24*, 6843).

The first two steps *via* transition states **TS1** and **TS2** involve sequential ligand coordination to the terminal borylene complex to form **Int2**. This is followed by concerted ligand addition to the Cr centre which proceeds *via* **TS3** leading to the free borylenes **3e** and **5**. The barrier to addition is much higher for CO (15.7 kcal mol^{-1}) than that for the more nucleophilic *t*BuNC (8.2 kcal mol^{-1}). For both CO and isonitrile addition, the overall reaction pathways are significantly exergonic, but much more so in the case of isonitrile. These calculations are in line with the observation that the isonitrile reactions achieve completion in relatively short times (<1 h) at room temperature, whereas the reaction with CO requires much more forcing conditions.

GFR 12 – A

[(SEE RULE 238 (1)]

FORM OF UTILIZATION CERTIFICATE FOR THE GRANTEE ORGANIZATION INCLUDING AUTONOMOUS ORGANIZATIONS

UTILIZATION CERTIFICATE FOR THE FINANCIAL YEAR 2018-19
(period from **April 01, 2018- May 30,2018**

In respect of recurring GRANT-IN-AID

1. Name of the scheme: Indo-German (DST-DAAD) joint research project entitled "Homocoupling, Heterocoupling and Liberation of Borylene Ligands"
2. Whether recurring or non-recurring grants: Recurring
3. Grants position at the beginning of the financial year
   (i) Cash in Hand/Bank Nil
   (ii) Unadjusted advances Nil
   (iii) Total Nil

4. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received year [figure as at Sl No 3(iii)]	Interest earned thereon	Interest deposited back to the government	Grant received during the year			Total Available funds (Rs.) (1+2-3+4) *including interest*	Expenditure incurred (Rs.)	Closing Balance (5-6)
1	2	3	4			5	6	7
			Sanction no. (i)	Date (ii)	Amount (Rs.) (iii)			
Nil	Nil	Nil	-	-	Nil	Nil	Nil	Nil

5. Component wise utilization of grants:

Grants-in-aid-General	Grant-in-aid -Salary	Grants-in-aid-creation of capital	Total
Nil	Nil	Nil	Nil

6. Details of grants position at end of the year
   (i) Cash in Hand /Bank : Nil
   (ii) Unadjusted Advance : Nil
   (iii) Total : Nil

7. Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled /are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets register) are maintained as prescribed in the relevant Act/Rules/standing instructions (mention the Act/Rules)

Finance Officer
Tezpur University

and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under. Indo-German (DST-DAAD) joint research project scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes give at Annexure- I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry /Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure—II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date:

Place:

Signature

Name
Chief Finance Officer
(Head of the Finance)

Finance Officer
Tezpur University

Signature

Name
Head of the Organisation

Registrar
Tezpur University

(TO BE FILLED IN BY DST)

2. Certified that I have satisfied myself that the conditions on which the grants-in-aid was sanctioned have been fulfilled/are being fulfilled and that I have exercised the following checks to see that the money was actually utilised for the purpose for which it was sanctioned:

Kinds of checks exercised.

1.
2.
3.
4.
5.

Signature
Designation
Date

Annexure - II

REQUEST FOR ANNUAL INSTALLMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE

(1st April, 2016 to 31st March, 2017)

1. Sanction Letter No.: INT/FRG/DAAD/P-9/2016
2. Total Project Cost Rs. 10,15,000/-
3. Sanctioned/Revised project cost (if applicable) Rs. N/A
4. Date of commencement of Project : 01-06-2016
5. Statement of Expenditure

	Month	Year

6. Grant Received in each year:

a.	I year	Rs .5,07,500/-
b.	II year	Rs. 2,34,084/-
c.	III year	Rs. N/A
d.	Interest, if any	Rs. 12,209/-
e.	Total	Rs.7,53,793/-

Note:

1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under the head, without prior approval of DST i.e. Figures in Column (vii) should not exceed corresponding figures in Column (iii)
2. Utilisation Certificate for each financial year ending 31st March has to be enclosed, along with request for carry-forward permission to next year

Finance Officer
Tezpur University

Annexure IInd Continued

Sl. No.	Sanctioned Heads**	Funds Allocated	Expenditure Incurred				Balance as on date (Col. iii - vii)	Required Funds till 31 March, 2019	Remarks (if any)
			I Yr.	II Yr.	III Yr.	Total (iv+v+vi)			
i.	ii.	iii.	iv.	v.	vi.	vii.	viii.	ix.	x.
1.	Salaries	-	-	-					
2.	Permanent Equipments	-	-	-	-				
3.	Supplies & Materials/consumables	-	-	-	-				
4.	Travel of Indian Scientists Abroad	4,68,584/-	1,81,942/-	1,99,890/-	-	3,81,832/-	86,752/-	Nil	
5.	Hospitality of Foreign Scientists - Per diem @ Rs.2,500 - Accommodation @ Rs.4,000/- per day	2,73,000/-	59,142/-	1,33,978/-	-	1,93,120/-	79,880/-	Nil	
6.	Contingencies	-	-	-	-				
7.	Overhead Expenses	-	-	-	-				
8.	Interest earned	12,209/-	-	-	-		12,209/-		
	Total	7,53,793/-	2,41,084/-	3,33,868/-		5,74,952/	**1,78,841/-***	Nil	

- *The balance amount of Rs. 1,78,841/- (Rupees One Lakh Seventy Eight Thousand Eight Hundred Forty One Only) was already returned vide* ***D. D. No.*** **454783** dated **07.08.2018.**

Name & Signature
Principal Investigator:
Date:

Prof. Ashwini Kr. Phukan
Ashwini Kr Phukan
23/10/2018

Signature of Competent financial authority
Date:

2/11/18
Finance Officer
Tezpur University