

Supporting Information for

**Unfolding the Crucial Role of a Nucleophile in a Ziegler-Natta Type Ir
Catalyzed Polyaminoborane Formation**

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S1. Computational Details:

All gas phase intermediates and transition state geometries were obtained using B3LYP [1] functional in GAUSSIAN09 package [2]. The effective core potential LANL2 along with LANL2DZ basis set was applied on Ir and for all other atoms Pople's 6-31+G(d,p) basis functions were employed. The intermediates are characterized by the presence of all real frequencies and transition states by single imaginary frequency and all real frequencies for the rest of the modes. Vibrational mode corresponding to each imaginary mode is analyzed carefully to confirm the nature of the transition state. Single point solvent phase calculation for THF are done in a CPCM [3] solvent model using M06L [4] functional employing same basis function on each atom with the gas phase optimized geometries in GAUSSIAN09 package [2]. Solvent phase enthalpies were computed by adding enthalpy corrections derived from gas phase to solvent phase energies at 1 atmospheric pressure and 298 K. Solvent phase free energies were obtained by adding gas phase free energy correction to the corresponding solvent phase total energies. Solvated species entropies cannot be estimated directly from the ideal phase model. However, based on standard practices the gas phase entropies obtained from the gas phase frequency computations were scaled by a scaling factor of 0.5 to account for the reduction of entropy of a species existing in gas phase as compared to its presence in the solution phase [5]. Solvent phase free energies were estimated by using the solvent phase enthalpies and the solvent phase entropies, i.e. the empirically scaled gas phase entropies.

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[4] Y. Zhao and D. G. Truhlar, "A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions," *J. Chem. Phys.*, 125 (2006), 194101: 1-18.

[5] (a) C. Spickermann, *Entropies of Condensed Phases and Complex Systems*, Springer Theses, Berlin, 2010, chap. 3, pp. 76 – 80, and references therein. (b) Wertz, D. H. *J. Am. Chem. Soc.* 1980, 102, 5316. (c) H. Li, X. Wang, F. Huang, G. Lu, J. Jiang, Z.-X. Wang, *Organometallics* 2011, 30, 5233–5247. (d) Y. Liang, S. Liu, Y. Z. Xia, Y. H. Li, Z.-X. Yu, *Chem. Eur. J.* 2008, 14, 4361.

S2. Interaction of NH_2BH_2 with IrH_2POCOP catalyst:

(a) Thermodynamically favoured product -

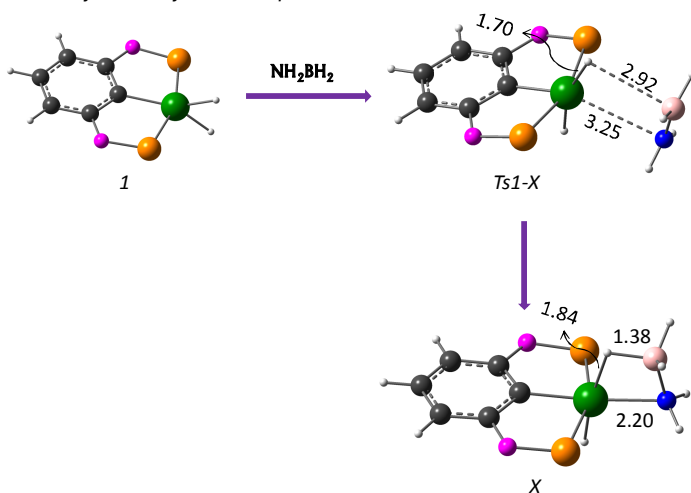


Figure 1. Pathway for formation of Thermodynamically favoured product X by interaction of NH_2BH_2 and IrH_2POCOP . Tertiary butyl groups on P are omitted for clarity. Color code: Ir green, P orange, O magenta, N blue, B pink, C grey, H white.

I.1

Ir	-0.00000200	-0.58843500	0.03410600
C	-0.00000900	1.47501100	-0.03889500
C	1.19987400	2.20265300	-0.06497800
C	-1.19990100	2.20263900	-0.06496400
C	1.22450900	3.59894100	-0.11495000
C	-1.22456200	3.59892500	-0.11493200
C	-0.00003000	4.27802700	-0.13857300
H	2.16683800	4.13609600	-0.13468700
H	-2.16689700	4.13606600	-0.13465300
H	-0.00003700	5.36405700	-0.17697700
P	-2.27497800	-0.18683700	0.00752100
P	2.27498600	-0.18681100	0.00751100
C	-3.22396800	-0.62726200	-1.58038900
C	-3.26242200	-0.51255500	1.60162600
C	3.22396100	-0.62726800	-1.58039300
C	3.26245300	-0.51251100	1.60160700
O	-2.40056000	1.51495000	-0.04148100
O	2.40053900	1.51498300	-0.04151000
H	-0.00000600	-1.98357600	0.83318900
H	0.00000200	-1.96335500	-0.77180400
C	-3.14786400	-2.15079600	-1.81566300
H	-3.60476400	-2.38178800	-2.78618900
H	-2.11272900	-2.50164500	-1.83378600
H	-3.68921200	-2.72106800	-1.05592400
C	-2.46909600	0.08925600	-2.72468100
H	-2.53117100	1.17679400	-2.63099300
H	-1.41297700	-0.19397300	-2.74883500
H	-2.92551400	-0.19708400	-3.68043500
C	-4.69230600	-0.16378200	-1.58824600
H	-5.09718600	-0.28841400	-2.60068000
H	-5.31701000	-0.75851100	-0.91636900
H	-4.78979400	0.89153900	-1.31811900
C	-2.31207000	-0.11498100	2.75583500
H	-1.39116400	-0.70386100	2.73955300
H	-2.04034500	0.94406100	2.70928300
H	-2.82331600	-0.29017100	3.71105500
C	-3.58860600	-2.01490700	1.71500900
H	-3.98741900	-2.21918700	2.71648000
H	-4.34834200	-2.32885200	0.99297000
H	-2.69811500	-2.63683900	1.57730500
C	-4.54785100	0.33034300	1.72199700
H	-5.32329000	0.02281000	1.01866900
H	-4.95514800	0.20471500	2.73341700
H	-4.34476200	1.39350300	1.57041400
C	2.31205500	-0.11509600	2.75583500
H	2.04026000	0.94393200	2.70937100
H	1.39118900	-0.70403500	2.73948300
H	2.82329600	-0.29033300	3.71105100
C	3.58878500	-2.01483500	1.71491900

H	3.98760700	-2.21912900	2.71638500
H	2.69836200	-2.63685500	1.57717500
H	4.34856200	-2.32865900	0.99287000
C	4.54780500	0.33049800	1.72205800
H	4.95512500	0.20479400	2.73345900
H	5.32326700	0.02311700	1.01868900
H	4.34461800	1.39365500	1.57059700
C	3.14788600	-2.15081300	-1.81561000
H	3.60479400	-2.38183200	-2.78612500
H	3.68924000	-2.72104700	-1.05584600
H	2.11275700	-2.50167900	-1.83372200
C	4.69229100	-0.16377000	-1.58828600
H	5.31700100	-0.75844600	-0.91636700
H	5.09717600	-0.28846800	-2.60071000
H	4.78976700	0.89157000	-1.31823100
C	2.46906500	0.08918000	-2.72471200
H	1.41294400	-0.19404500	-2.74880900
H	2.53115300	1.17672300	-2.63110500
H	2.92545100	-0.19723500	-3.68045900

II. Ts1X

Ir	-0.00000900	-0.38773000	-0.01122500
C	-0.00000400	1.57985700	-0.42675600
C	1.19499800	2.29808200	-0.56084000
C	-1.19500200	2.29808200	-0.56086600
C	1.21652500	3.67040000	-0.81109000
C	-1.21652800	3.67040000	-0.81111400
C	0.00000000	4.35081400	-0.93775300
H	2.16669300	4.18683900	-0.90129200
H	-2.16669400	4.18683800	-0.90133400
H	0.00000200	5.41928100	-1.13070300
P	-2.29670300	-0.00147500	0.02920800
P	2.29669900	-0.00148200	0.02921300
C	-3.45505000	-0.78152600	-1.27573400
C	-3.12583100	0.08684400	1.74608400
C	3.45503800	-0.78151100	-1.27575700
C	3.12585200	0.08683400	1.74607600
O	-2.39948100	1.61578300	-0.44112100
O	2.39947300	1.61578700	-0.44107800
N	-0.00004500	-3.55207200	-0.75641300
H	-0.84245300	-3.42160500	-1.29767100
H	0.84226700	-3.42162100	-1.29782900
H	0.00000900	-1.13290700	1.52053900
B	0.00010200	-3.90019500	0.60098800
H	1.04458400	-4.07019500	1.15403600
H	-1.04424600	-4.07019200	1.15429000
C	4.67081400	0.11038400	-1.61042600
H	5.21201300	-0.34268800	-2.45077100
H	4.35786600	1.11336700	-1.91007200
H	5.37282000	0.20279200	-0.78146200

C	3.93084600	-2.17086900	-0.80440600
H	3.10322900	-2.80823400	-0.47404600
H	4.43173300	-2.68027600	-1.63694500
H	4.65037300	-2.10413700	0.01594500
C	2.62892500	-0.94400400	-2.57132800
H	1.77349800	-1.60984300	-2.43548000
H	2.24265600	0.01440200	-2.92968200
H	3.27625300	-1.36358800	-3.35154100
C	2.29516600	1.11067900	2.55397800
H	1.24388900	0.81655400	2.60891700
H	2.69195500	1.15259300	3.57587200
H	2.35632800	2.11473100	2.12570600
C	3.03300500	-1.28194700	2.45115600
H	3.39812200	-1.17170200	3.47999200
H	2.00035000	-1.63743600	2.49316700
H	3.64489700	-2.04895800	1.96956000
C	4.58955900	0.56562800	1.70798300
H	4.92639400	0.74737300	2.73639400
H	5.26131900	-0.18283800	1.27909100
H	4.70070000	1.50144700	1.15257800
C	-2.29511400	1.11066800	2.55398100
H	-1.24383200	0.81655200	2.60886300
H	-2.35630500	2.11473500	2.12574400
H	-2.69185600	1.15254700	3.57589400
C	-3.03299000	-1.28195100	2.45114000
H	-2.00034700	-1.63748500	2.49307100
H	-3.39802700	-1.17170500	3.48000400
H	-3.64495200	-2.04892700	1.96957700
C	-4.58953100	0.56566300	1.70802900
H	-5.26131800	-0.18279600	1.27916500
H	-4.92633200	0.74742300	2.73644900
H	-4.70067200	1.50148000	1.15262000
C	-3.93081000	-2.17089300	-0.80436600
H	-4.65040200	-2.10417000	0.01592900
H	-4.43160200	-2.68036700	-1.63692000
H	-3.10317700	-2.80819500	-0.47391600
C	-4.67084800	0.11034700	-1.61037400
H	-5.21209500	-0.34276700	-2.45066500
H	-5.37280600	0.20279200	-0.78137300
H	-4.35792000	1.11331700	-1.91008500
C	-2.62896900	-0.94401100	-2.57132800
H	-2.24267500	0.01439200	-2.92966400
H	-1.77356200	-1.60988500	-2.43552100
H	-3.27633000	-1.36355200	-3.35153700
H	-0.00002000	-0.23869300	-1.61704400

III. X

C	-1.18227600	2.28320000	-0.34158100
C	0.00003800	1.53541300	-0.29283200
C	1.18234500	2.28323300	-0.34138300

C	1.21347700	3.67054800	-0.49121300
C	0.00002700	4.36027200	-0.57536100
C	-1.21341800	3.67051600	-0.49141300
Ir	0.00009000	-0.49727000	-0.02507900
B	0.00000100	-2.51798900	-1.50772700
N	-0.00058300	-2.69737900	0.02220300
O	2.39627600	1.61345000	-0.21819800
P	2.32126800	-0.04177400	0.03488300
C	3.12167400	-0.21693300	1.76797200
O	-2.39623300	1.61340200	-0.21860600
P	-2.32125900	-0.04175100	0.03484000
C	-3.12160100	-0.21651300	1.76799900
C	3.52403200	-0.56779800	-1.35687500
C	-3.52415000	-0.56802500	-1.35671700
C	4.64500800	0.00626900	1.81400300
C	2.46723700	0.84233700	2.68309600
C	2.79465700	-1.62749700	2.30394400
C	4.79883700	0.30596800	-1.41397200
C	3.90518100	-2.05386900	-1.20432900
C	2.77332400	-0.35184700	-2.69205500
H	2.16534300	4.18990800	-0.53166600
H	0.00002600	5.43960500	-0.69445600
H	-2.16529500	4.18984600	-0.53201800
C	-2.79483800	-1.62704100	2.30419900
C	-2.46690400	0.84279000	2.68289700
C	-4.64490400	0.00694300	1.81396900
C	-2.77366700	-0.35210700	-2.69203900
C	-3.90519600	-2.05409700	-1.20392700
C	-4.79905000	0.30560100	-1.41369100
H	0.00017900	-0.16036400	1.52527800
H	-0.00014000	-1.15921900	-1.73881500
H	-1.01380100	-2.88618800	-2.03961700
H	1.01436700	-2.88608100	-2.03859600
H	0.82106900	-3.12209900	0.43382300
H	-0.82286200	-3.12139600	0.43329200
H	-4.51425100	-2.35627900	-2.06499000
H	-3.02672400	-2.70460000	-1.18659400
H	-4.50175800	-2.23827800	-0.30507000
H	-5.31787700	0.08595600	-2.35510600
H	-5.50010700	0.10120300	-0.60531400
H	-4.55597800	1.37097700	-1.40819600
H	-3.44919700	-0.62231600	-3.51312900
H	-2.49142000	0.69679200	-2.82504200
H	-1.87935400	-0.96686100	-2.77335100
H	-4.96762700	-0.02430900	2.86229000
H	-4.92701100	0.98342400	1.41187800
H	-5.20073100	-0.76912800	1.28253500
H	-3.21119700	-1.73420900	3.31367200
H	-3.23313400	-2.41945100	1.68759600
H	-1.71535000	-1.78806900	2.36547600
H	-2.84492900	0.70303800	3.70334200
H	-1.37927000	0.75154300	2.70935400

H	-2.71809800	1.85734900	2.36255600
H	2.84513600	0.70220600	3.70353700
H	2.71877600	1.85689900	2.36302800
H	1.37957200	0.75143400	2.70944900
H	3.21122400	-1.73500400	3.31329500
H	1.71513700	-1.78822800	2.36541700
H	3.23256400	-2.41990000	1.68705700
H	4.96774300	-0.02548600	2.86230600
H	5.20073000	-0.76964400	1.28222600
H	4.92723500	0.98289500	1.41235100
H	4.51405600	-2.35593200	-2.06556200
H	4.50193500	-2.23813500	-0.30562300
H	3.02673000	-2.70439200	-1.18686100
H	5.31763100	0.08632400	-2.35540500
H	4.55563600	1.37131600	-1.40852100
H	5.49996900	0.10171600	-0.60563100
H	3.44877400	-0.62182600	-3.51328600
H	1.87911100	-0.96676700	-2.77328100
H	2.49084400	0.69701000	-2.82490300

(b) *Kinetically favoured product -*

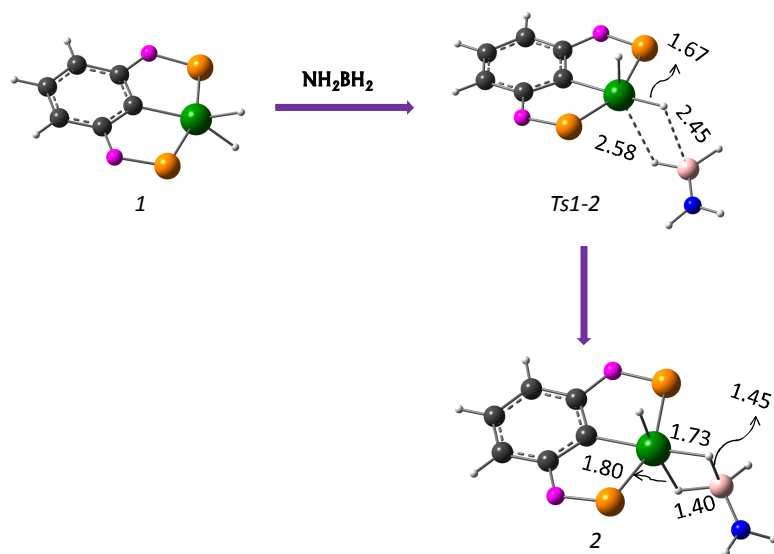


Figure 2. Pathway for formation of Kinetically favoured complex 2 by interaction of NH_2BH_2 and IrH_2POCOP . Tertiary butyl groups on P are omitted for clarity. Color code: Ir green, P orange, O magenta, N blue, B pink, C grey, H white.

I. Ts1-2

Ir	-0.00641400	0.42693200	0.19320600
C	-0.06167400	-1.39789900	-0.83172500
C	1.10618300	-2.09977700	-1.15069800
C	-1.26813100	-2.04567200	-1.11946300
C	1.10186900	-3.34152600	-1.78998200
C	-1.33495700	-3.28654400	-1.75792500
C	-0.13465900	-3.92085100	-2.09936400
H	2.03482500	-3.84334900	-2.02538500

H	-2.29532800	-3.74569900	-1.96892500
H	-0.16311200	-4.88588100	-2.59733000
P	-2.31863800	0.03155700	0.10235200
P	2.26495300	-0.11248300	0.10880400
C	-3.11497000	-0.41358300	1.78050200
C	-3.50081400	1.04487300	-1.00522400
C	3.01992500	-0.67417500	1.77273500
C	3.50969400	0.89136300	-0.93156400
O	-2.45600600	-1.43653700	-0.72879800
O	2.33159900	-1.54426300	-0.78751200
H	0.01160800	2.49019000	-1.34389200
H	0.04124200	1.83849400	1.08023100
H	-0.03281200	-0.20825000	1.58793300
B	-0.04505100	3.51025900	-0.70514000
H	-1.06173600	3.87668400	-0.20676500
C	-2.85528700	0.74348100	2.77006300
H	-3.24981600	0.46344700	3.75518500
H	-1.78868200	0.95816500	2.86971900
H	-3.35427900	1.66868300	2.46669600
C	-2.41335900	-1.69261400	2.29217800
H	-2.59315000	-2.54400500	1.63027300
H	-1.33391400	-1.56282500	2.39302800
H	-2.81626400	-1.93784900	3.28254100
C	-4.62675500	-0.70761900	1.71756000
H	-4.95198600	-1.06171700	2.70405100
H	-5.21721700	0.18214800	1.48581100
H	-4.86477200	-1.48995200	0.99142400
C	-2.70985000	1.34397200	-2.29958700
H	-1.82831900	1.95678900	-2.11343100
H	-2.39595300	0.42294000	-2.80087700
H	-3.36111500	1.89367700	-2.99056900
C	-3.88564700	2.36640200	-0.31345500
H	-4.42829700	2.99923500	-1.02707500
H	-4.54642400	2.20411400	0.54356200
H	-3.00895300	2.92483400	0.02440800
C	-4.77003000	0.26678700	-1.41716000
H	-5.47032500	0.12166600	-0.59517300
H	-5.29103100	0.84783200	-2.18892100
H	-4.52169800	-0.70924500	-1.84033200
C	2.75134600	1.29469800	-2.21700500
H	2.42240600	0.41475800	-2.77851900
H	1.87457800	1.91020600	-2.01136100
H	3.42782000	1.86743900	-2.86414300
C	3.93721400	2.15125900	-0.15424300
H	4.49041100	2.82147100	-0.82529500
H	3.07749500	2.69849300	0.24494000
H	4.60351500	1.91133900	0.67975500
C	4.74885100	0.08292500	-1.37364900
H	5.30768100	0.68094600	-2.10516700
H	5.42959700	-0.14280700	-0.55345300
H	4.46136900	-0.85484600	-1.85490100
C	2.82136300	0.44825900	2.81425300

H	3.18094600	0.09565800	3.78925900
H	3.38455300	1.35194200	2.56361200
H	1.76981400	0.72791900	2.91172400
C	4.51131600	-1.05453700	1.70048100
H	5.15376400	-0.18998900	1.51592800
H	4.81013000	-1.47719800	2.66806800
H	4.70667400	-1.81097500	0.93516900
C	2.23703100	-1.93043000	2.21747000
H	1.16600300	-1.74072200	2.31181500
H	2.37457500	-2.75970500	1.51855200
H	2.61123700	-2.24560000	3.19939200
N	1.05247500	4.37965800	-0.72141400
H	1.93319900	4.17001600	-1.16765700
H	1.04217500	5.27638600	-0.25719700

II. 2

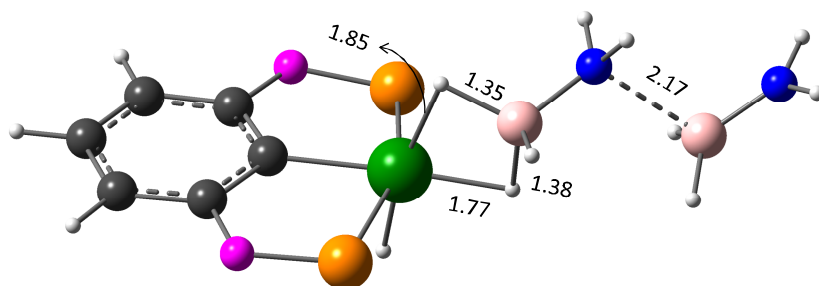
Ir	0.00904800	-0.48429200	0.09637900
C	0.03901300	1.46959200	-0.58543800
C	-1.13250000	2.19518200	-0.81540500
C	1.23191900	2.17723100	-0.75655800
C	-1.14449500	3.52098200	-1.25243800
C	1.28369100	3.50295400	-1.19196700
C	0.08017500	4.16737400	-1.44840300
H	-2.08789100	4.02924300	-1.42278200
H	2.24171700	3.99710200	-1.31575900
H	0.09636900	5.19816600	-1.78980900
P	2.34270500	-0.04776200	0.07685100
P	-2.29955500	0.02614700	0.07669900
C	3.15678100	0.08478300	1.80238000
C	3.54468500	-0.82832400	-1.19952800
C	-3.09026500	0.31331300	1.79588100
C	-3.54532600	-0.79818000	-1.12260900
O	2.43209300	1.53799800	-0.46593500
O	-2.35297200	1.57130000	-0.57957800
H	0.02694500	-1.53351800	-1.36498700
H	0.01277100	-2.07798600	0.76902800
H	0.00913500	0.22736300	1.51444700
B	0.15109200	-2.66239400	-0.54837200
H	1.25617400	-3.11153000	-0.64343500
C	2.90427000	-1.23870200	2.55641600
H	3.31613900	-1.15616100	3.56999600
H	1.83563900	-1.45291100	2.63775300
H	3.38688600	-2.09422400	2.07397800
C	2.46099800	1.24230200	2.55331600
H	2.63887000	2.20383800	2.06383600
H	1.38304200	1.09221500	2.63361700
H	2.87351800	1.29417500	3.56844200
C	4.66656100	0.39631000	1.77969100
H	5.00377500	0.54493200	2.81325500
H	5.26296300	-0.41755000	1.36201700

H	4.88486600	1.31483500	1.22805900
C	2.74802400	-1.01673100	-2.51119500
H	1.96575700	-1.76831100	-2.41555300
H	2.28698800	-0.08174100	-2.84491700
H	3.44387200	-1.34363700	-3.29379700
C	4.07561300	-2.19437700	-0.71875500
H	4.65066500	-2.65297400	-1.53308200
H	4.74818000	-2.10062700	0.13806600
H	3.27069000	-2.88403300	-0.45556200
C	4.73228200	0.10957200	-1.52060300
H	5.41196100	0.24928300	-0.68059400
H	5.30853100	-0.34578200	-2.33565500
H	4.38972800	1.09077800	-1.85560000
C	-2.76446800	-1.13270900	-2.41483200
H	-2.30004000	-0.23827700	-2.84107600
H	-1.98390800	-1.87819200	-2.26232900
H	-3.47185600	-1.52639900	-3.15534600
C	-4.13804200	-2.08453400	-0.50952100
H	-4.62184600	-2.67145500	-1.29963000
H	-3.38628700	-2.72210000	-0.03533100
H	-4.89768700	-1.86637600	0.24576800
C	-4.69474100	0.15443500	-1.52667900
H	-5.30964600	-0.35604800	-2.27858900
H	-5.34805000	0.42061900	-0.69613900
H	-4.31070700	1.07470600	-1.97102700
C	-2.89167000	-0.96064300	2.64458500
H	-3.25329200	-0.77180900	3.66312600
H	-3.45191000	-1.81510900	2.25267100
H	-1.83679600	-1.24097800	2.70326700
C	-4.58508600	0.69025300	1.75806900
H	-5.22046300	-0.12119200	1.39669100
H	-4.90929400	0.92021200	2.78077700
H	-4.76586000	1.58022200	1.14876800
C	-2.33973200	1.49081600	2.45877800
H	-1.27154800	1.29367200	2.56268600
H	-2.46490700	2.41761200	1.89248400
H	-2.75610100	1.64550200	3.46172700
N	-0.85000900	-3.67211800	-0.79272700
H	-1.84669900	-3.54907600	-0.73090100
H	-0.57883400	-4.62472900	-0.97905100

S3. Optimized geometries of Intermediates and Transition states with coordinates for chain propagation and termination of Polyaminoborane:

Note: Tertiary butyl groups on P atoms are omitted for clarity. Dotted bond indicate H-bonding and Bond making or breaking for Intermediate and transition state respectively.

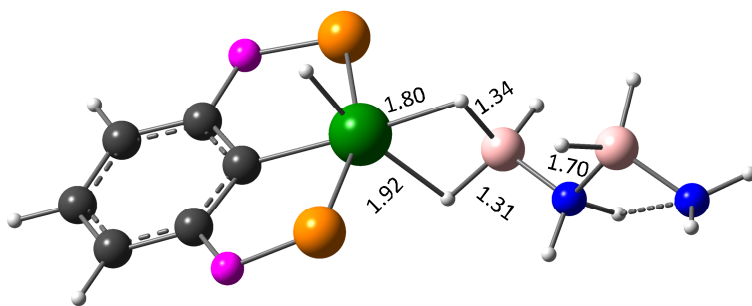
1. Ts2-3



Ir	-0.04844000	0.21516400	0.01383400
C	-0.39057400	-1.76517200	-0.43272700
C	0.65246600	-2.68217000	-0.59356600
C	-1.68318900	-2.29330300	-0.51197700
C	0.44912200	-4.03195100	-0.88594100
C	-1.94606600	-3.63398200	-0.79995800
C	-0.86460500	-4.49828700	-0.99670100
H	1.29871000	-4.69485300	-1.01228300
H	-2.97076100	-3.98565100	-0.85932300
H	-1.04675800	-5.54415900	-1.22516300
P	-2.42256400	0.15629400	0.06538900
P	2.15933000	-0.64016300	0.05432200
C	-3.19643300	0.35794900	1.80092000
C	-3.51704300	0.95891800	-1.28836400
C	2.90529800	-0.86064200	1.80022400
C	3.49699100	-0.15124800	-1.22078200
O	-2.76396700	-1.45028900	-0.27999800
O	1.95891800	-2.23320700	-0.43892800
H	0.08606200	1.20129100	-1.55142700
H	0.20879900	1.89741100	0.48690200
H	-0.13342500	-0.35303700	1.47681900
B	0.12655500	2.33654700	-0.81973100
H	-0.89747600	2.94122700	-0.95211800
C	-2.74049400	1.71550500	2.37748900
H	-3.11842300	1.81197300	3.40292900
H	-1.65074900	1.79315500	2.40789700
H	-3.12477000	2.56455200	1.80484900
C	-2.65016500	-0.78326200	2.68810100
H	-2.93136100	-1.76644500	2.30098900
H	-1.56350200	-0.74778500	2.78281100
H	-3.07883800	-0.67619700	3.69185600
C	-4.73540100	0.26401000	1.82645800
H	-5.06554800	0.30516300	2.87186600

H	-5.22016900	1.09142900	1.30433900
H	-5.09347800	-0.67947100	1.40500000
C	-2.72443100	0.87723100	-2.61360300
H	-1.83781800	1.51010200	-2.60461500
H	-2.41358500	-0.14791100	-2.83931900
H	-3.37732500	1.21442700	-3.42809300
C	-3.82889300	2.43496600	-0.96674600
H	-4.34194800	2.87933100	-1.82888200
H	-4.49336700	2.54307400	-0.10538000
H	-2.92495000	3.01981900	-0.78361600
C	-4.83522700	0.17768700	-1.49890200
H	-5.50506700	0.21953400	-0.64071700
H	-5.36197500	0.63090700	-2.34783400
H	-4.64672700	-0.87087000	-1.73808600
C	2.75727400	0.12576500	-2.55107700
H	2.17855600	-0.74522700	-2.87365200
H	2.07535600	0.97491900	-2.49678700
H	3.50280300	0.33836900	-3.32702500
C	4.26293200	1.10717200	-0.76036000
H	4.81741600	1.52242200	-1.61100200
H	3.61177900	1.89256000	-0.36739100
H	4.99403600	0.87666800	0.01937000
C	4.49806600	-1.29661300	-1.50159000
H	5.15657300	-0.97861400	-2.31973100
H	5.13251800	-1.53413000	-0.64820800
H	3.98457500	-2.20800700	-1.81479300
C	2.88944500	0.50750900	2.51419000
H	3.25746300	0.37742700	3.53959000
H	3.53112000	1.24603700	2.02577000
H	1.88075200	0.92467400	2.56437800
C	4.33344500	-1.44173800	1.81071200
H	5.06916400	-0.76612100	1.36974500
H	4.63140500	-1.60477600	2.85388600
H	4.38588900	-2.40716800	1.29959800
C	2.00242000	-1.85269600	2.56827800
H	0.97154200	-1.50273400	2.64520000
H	1.99588300	-2.84039000	2.09934900
H	2.39794400	-1.96118100	3.58545300
N	1.29484200	3.21531300	-1.09888600
H	1.10394700	3.97244300	-1.74512300
H	2.18173500	2.79497900	-1.34527100
B	1.88497300	4.46410800	0.57656900
H	2.59921200	3.61800800	1.04561400
H	0.76952400	4.59628600	0.99760100
N	2.51870000	5.61962600	0.01027700
H	3.50820500	5.67983500	-0.17542200
H	2.02374800	6.47335100	-0.19845600

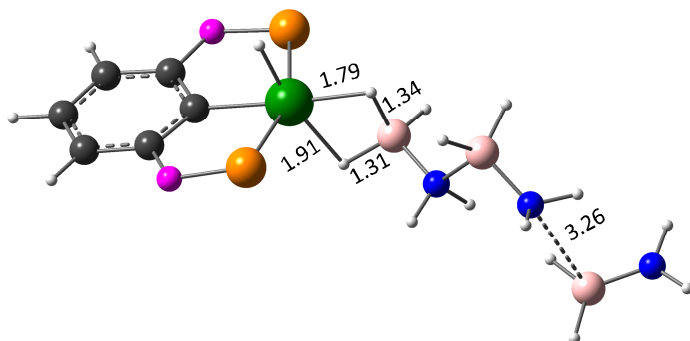
2.3



Ir	-0.05461300	0.21563500	0.03969100
C	-0.39567900	-1.74848100	-0.44322200
C	0.64910400	-2.65412400	-0.65484700
C	-1.68837300	-2.28169300	-0.49259300
C	0.44296500	-3.99712500	-0.97457400
C	-1.95136600	-3.61651500	-0.80568800
C	-0.87109500	-4.46798200	-1.05718000
H	1.29170500	-4.65203900	-1.14113400
H	-2.97512000	-3.97377800	-0.84160000
H	-1.05430500	-5.50898800	-1.30580400
P	-2.43085700	0.16762700	0.08023700
P	2.16107000	-0.63621200	0.05130900
C	-3.22340800	0.43956200	1.79163100
C	-3.49741000	0.91559200	-1.32645500
C	2.89042800	-0.93222000	1.79188700
C	3.49906800	-0.08206200	-1.19197000
O	-2.76496900	-1.45254600	-0.20192200
O	1.95638800	-2.20284000	-0.52101400
H	0.08370000	1.37054500	-1.48866500
H	0.21062000	1.91148200	0.56936600
H	-0.14382300	-0.41902100	1.46140600
B	0.09753100	2.39467600	-0.67396000
H	-0.92004500	3.01548800	-0.75995800
C	-2.82419400	1.84336700	2.29652200
H	-3.20553300	1.97416300	3.31666500
H	-1.73905400	1.97241300	2.32261200
H	-3.24420200	2.64566600	1.68415800
C	-2.64216500	-0.62764100	2.74667100
H	-2.86009200	-1.64284700	2.40347500
H	-1.56176200	-0.52675400	2.86733600
H	-3.10222500	-0.49497500	3.73315400
C	-4.75805000	0.28882600	1.80162200
H	-5.10590000	0.36778200	2.83891600
H	-5.26330000	1.07268300	1.23349600
H	-5.07476000	-0.68618700	1.42052500
C	-2.66377200	0.80019300	-2.62364900
H	-1.79360400	1.45615800	-2.61308400
H	-2.32001200	-0.22443900	-2.79910400

H	-3.29804400	1.08864300	-3.47065400
C	-3.84102800	2.39661600	-1.06789400
H	-4.33139700	2.80120000	-1.96208300
H	-4.53662900	2.52320000	-0.23408000
H	-2.95332400	3.00291700	-0.87557700
C	-4.79829600	0.10771400	-1.54356000
H	-5.48441000	0.15858800	-0.69840900
H	-5.31582200	0.53333300	-2.41206300
H	-4.59002800	-0.94307600	-1.75427700
C	2.76639900	0.23912400	-2.51585200
H	2.21752300	-0.63102600	-2.88921100
H	2.05862300	1.06431800	-2.42897000
H	3.51303000	0.51279100	-3.27076800
C	4.23910100	1.16677400	-0.66879700
H	4.79675800	1.62795500	-1.49286100
H	3.57236300	1.92483200	-0.24851900
H	4.96473000	0.91192000	0.10863200
C	4.51602900	-1.20287600	-1.51089100
H	5.17037900	-0.84742000	-2.31669500
H	5.15373000	-1.45883700	-0.66550500
H	4.01696200	-2.11085800	-1.85622600
C	2.86931700	0.40328000	2.56532600
H	3.23191500	0.22605400	3.58547400
H	3.51037500	1.16529800	2.11440000
H	1.86034700	0.81754000	2.62994200
C	4.31873900	-1.51286400	1.78517700
H	5.05588300	-0.81584000	1.38176200
H	4.60923900	-1.72409900	2.82164900
H	4.37662200	-2.45337700	1.22987300
C	1.98198200	-1.95694000	2.50913000
H	0.95091500	-1.61026900	2.60051800
H	1.97553600	-2.92286600	1.99691400
H	2.37313700	-2.11240900	3.52175500
N	1.29551600	3.32086900	-0.92420800
H	1.05947400	4.02499000	-1.62236600
H	2.12732200	2.85996500	-1.28514600
B	1.82667200	4.25651500	0.39452300
H	2.37411900	3.43886600	1.11513400
H	0.79769900	4.69811700	0.86906200
N	2.75213900	5.30291400	-0.17589600
H	3.72727600	5.24909200	0.08988600
H	2.44964500	6.26550600	-0.09608800

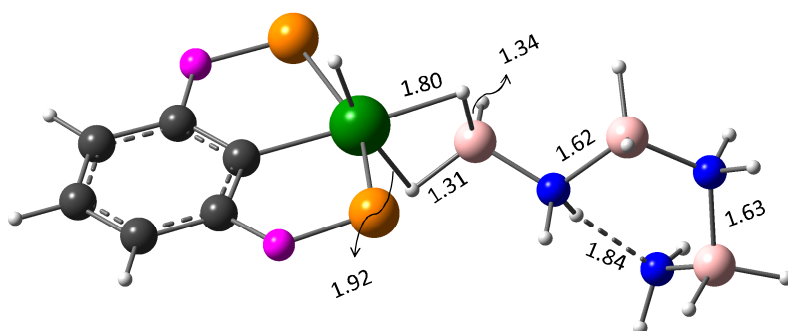
3. Ts3-4



Ir	-0.20945100	-0.03108000	0.14760800
C	-1.60071800	-1.22334700	-0.77559500
C	-1.32717500	-2.55110600	-1.12155700
C	-2.90666700	-0.78542900	-1.01885700
C	-2.25832600	-3.38761700	-1.73936900
C	-3.87672600	-1.57858000	-1.63453200
C	-3.53587700	-2.88389100	-2.00188900
H	-1.98669600	-4.40634800	-1.99517800
H	-4.87104000	-1.18140600	-1.80944300
H	-4.27487100	-3.51703000	-2.48368100
P	-2.08212200	1.43642700	0.10597000
P	0.98007100	-2.08339700	0.03128000
C	-2.85886200	1.80763500	1.80826500
C	-2.19065800	2.95155600	-1.06625000
C	1.14860200	-3.01629100	1.68908400
C	2.51726500	-2.32114100	-1.07912700
O	-3.26804900	0.49483800	-0.61708100
O	-0.07614100	-3.07294600	-0.82096100
H	0.82298200	1.00222000	-1.08202700
H	0.95752100	0.99137200	1.04642500
H	-0.89298100	-0.68126200	1.39122700
B	1.36126500	1.62849800	-0.06274400
H	0.98297700	2.76098300	-0.02145200
C	-1.79034700	2.47759500	2.69963200
H	-2.21600300	2.64358900	3.69692700
H	-0.90412600	1.84784600	2.81243400
H	-1.46832300	3.44910600	2.31456500
C	-3.27060000	0.45728400	2.43726600
H	-4.00905200	-0.06803700	1.82529900
H	-2.41567900	-0.20365700	2.59101100
H	-3.71998200	0.65608500	3.41772700
C	-4.12067000	2.69159400	1.74262700
H	-4.53850400	2.77219000	2.75358400
H	-3.90817200	3.70650400	1.40067700
H	-4.89144100	2.25576400	1.10063200
C	-1.37787900	2.59862000	-2.33332200

H	-0.30943800	2.53079800	-2.13150200
H	-1.70663900	1.65451600	-2.77993500
H	-1.53425700	3.38985900	-3.07656900
C	-1.60372000	4.22144100	-0.41655300
H	-1.57900700	5.01833000	-1.17026500
H	-2.21378200	4.58285200	0.41561600
H	-0.58188300	4.07303900	-0.06087300
C	-3.64641500	3.21844400	-1.51566800
H	-4.30153300	3.52314000	-0.70001900
H	-3.62683500	4.03781400	-2.24491200
H	-4.08420200	2.34395800	-2.00097900
C	2.31664100	-1.40789100	-2.31074100
H	1.40578100	-1.66768800	-2.85919600
H	2.25715000	-0.34940700	-2.05528900
H	3.16581800	-1.54578000	-2.99059500
C	3.80574000	-1.92954200	-0.32521800
H	4.62380100	-1.81431700	-1.04634700
H	3.71983900	-0.99482100	0.23528200
H	4.10993000	-2.70180100	0.38631600
C	2.64287100	-3.76710900	-1.61237100
H	3.48028900	-3.79492800	-2.32071000
H	2.85320600	-4.49553500	-0.83009500
H	1.74046900	-4.07916600	-2.14232000
C	1.86960300	-2.09726100	2.69741700
H	1.90666800	-2.60129500	3.67110800
H	2.89714300	-1.86851500	2.40411200
H	1.34570800	-1.14699800	2.82546700
C	1.89037200	-4.36383400	1.57981900
H	2.94442700	-4.24650800	1.31949100
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H	1.41805400	-5.03493900	0.85666900
C	-0.27916800	-3.31607000	2.19935800
H	-0.86645300	-2.40836000	2.35079400
H	-0.82678300	-3.97094400	1.51628800
H	-0.19776800	-3.82569200	3.16687600
N	2.89289200	1.59206500	-0.10109600
H	3.25328800	2.37554000	-0.64627600
H	3.28711600	0.76374800	-0.54003400
B	3.69745100	1.75486500	1.38481200
H	3.49808900	0.68376000	1.93294100
H	3.12650400	2.68035700	1.92960800
N	5.14644200	2.02809300	1.05482900
H	5.81640300	1.30819300	1.29552700
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B	5.67313700	3.95712400	-1.51968200
H	4.48756600	3.90558400	-1.68594000
H	6.41195600	3.14630400	-1.99096400
N	6.20203400	5.05520300	-0.83347700
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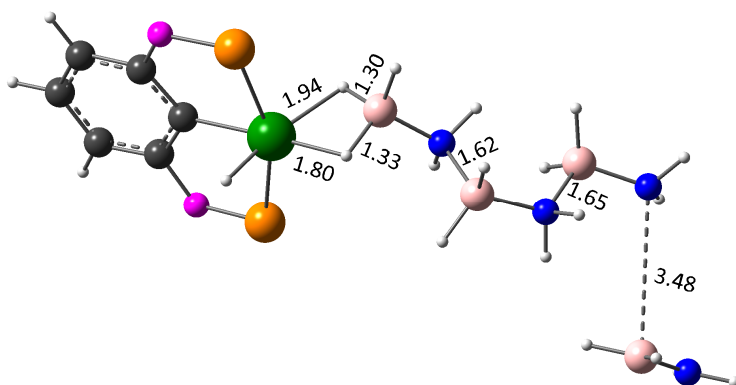
4. 4



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C	-1.05968200	-3.89517700	-1.64744200
C	-3.15322500	-2.66311600	-1.62384600
C	-2.42363900	-3.81219500	-1.94309700
H	-0.48521100	-4.78952400	-1.86440900
H	-4.21732900	-2.59305500	-1.82306000
H	-2.92418200	-4.65375300	-2.41243000
P	-2.41228600	0.78127000	0.08452400
P	1.60310000	-1.60279000	0.08045400
C	-3.26534700	0.85514000	1.78959100
C	-3.00102700	2.19612100	-1.06612400
C	2.05196600	-2.36397400	1.77383900
C	3.14031300	-1.40413500	-1.03646600
O	-3.22825700	-0.47646400	-0.66804200
O	0.90221700	-2.90619300	-0.71184500
H	0.49025200	1.26498300	-1.12733400
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H	-0.61193400	-0.81793800	1.39969100
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C	-3.25209800	-0.57230000	2.38304200
H	-3.81253500	-1.27566500	1.76110900
H	-2.23998500	-0.95951500	2.51473200
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H	-5.15569100	1.23414000	2.75217500
H	-4.83984200	2.36252700	1.43915800
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H	-1.09655100	2.32920800	-2.16835700

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C	-2.80881300	3.57876600	-0.41097700
H	-3.04300000	4.35195100	-1.15316900
H	-3.48054000	3.73299200	0.43790400
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H	-5.18139600	2.14880900	-0.66439900
H	-4.70791400	2.78377000	-2.23722100
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C	2.66923700	-0.64544100	-2.29858800
H	1.88343100	-1.19355600	-2.82783600
H	2.28646200	0.35122600	-2.07817700
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C	4.24956900	-0.60765600	-0.31750800
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H	2.66703000	-1.64994800	3.72059300
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H	1.65840500	-0.48666100	2.84258800
C	3.17247500	-3.42132500	1.70825100
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5. Ts4-5

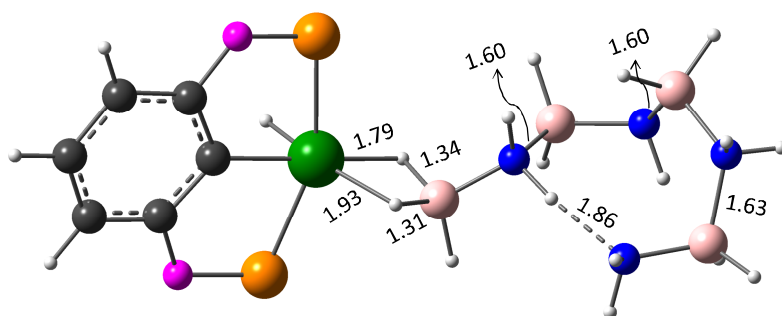


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C	4.01350600	3.11453400	-1.52367200
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H	5.40791500	1.46412400	-1.29977000
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P	2.57562100	-1.40851300	0.11551300
P	-0.61871400	1.99571700	0.03253500
C	3.18031600	-1.94131300	1.84255700
C	2.86339600	-2.77968200	-1.19728000
C	-0.93342600	2.80638700	1.73365800
C	-2.08841100	2.25307600	-1.15940600
O	3.78424800	-0.35415200	-0.37594100
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H	-0.42634100	-2.84868400	-0.33098600
C	2.04741100	-2.73626300	2.52812000
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C	-2.23525000	3.72603900	-1.60632200
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6. 5

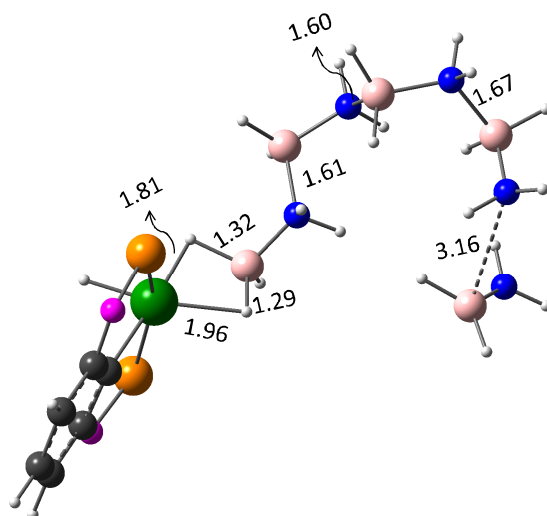


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C	3.38926500	-0.91326900	2.43931300
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7. Ts5-6

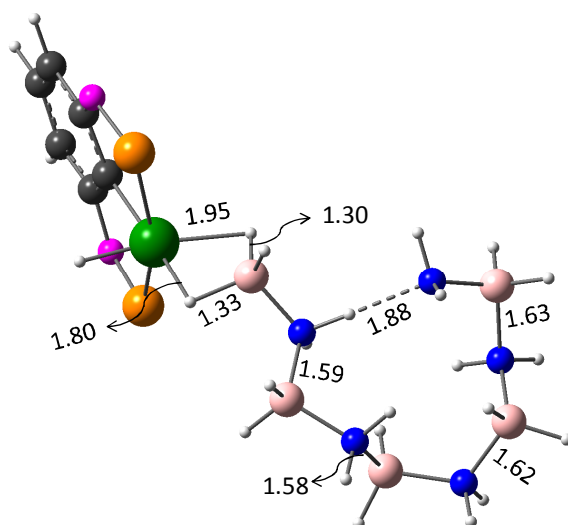


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H	0.30350000	3.91428700	0.38231700
C	-2.74621700	4.27847600	-1.28882000
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8. 6

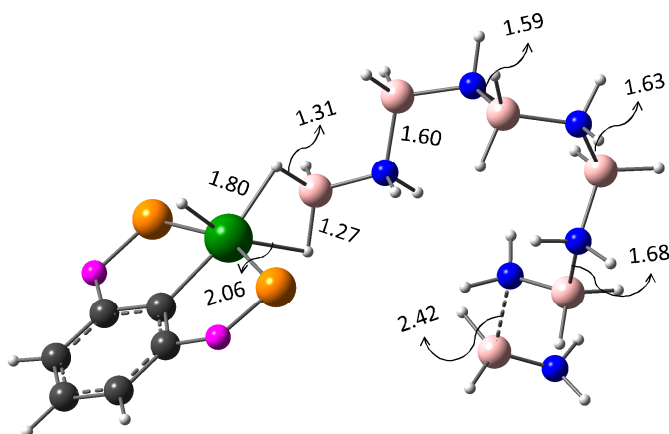


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H	2.18721800	-2.86131000	3.82869700
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9. Ts6-7

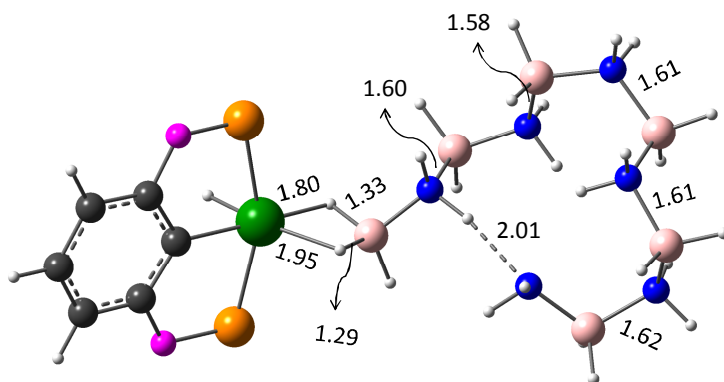


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10. 7

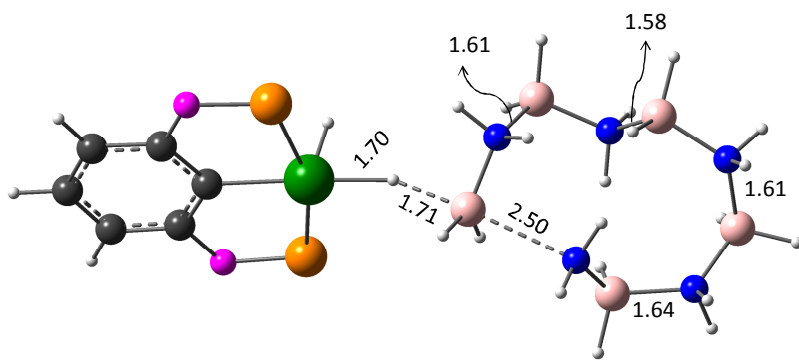


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C	2.77568200	3.15820500	1.75210000

H	2.92917900	2.10558400	1.99789800
H	3.46288300	3.42699900	0.94538600
H	3.04240300	3.74910000	2.63649800
N	-2.47421700	-0.09898000	0.49132500
H	-3.15496800	-0.69951600	-0.02295600
H	-2.50862600	0.80077900	0.01697500
B	-2.98683700	0.09446000	1.99062000
H	-2.46565700	1.07518600	2.46787300
H	-2.76562800	-0.91570900	2.61609100
N	-4.57179800	0.32255300	1.93094700
H	-4.87840700	0.36760000	2.90320100
H	-5.00707600	-0.52704600	1.56325400
B	-5.09215100	1.59557700	1.14669000
H	-4.81223400	2.58992800	1.77770000
H	-4.61586200	1.61139200	0.03165200
N	-6.67985100	1.49747300	0.97924400
H	-7.13580700	1.65569800	1.87922300
H	-6.96133300	2.30455900	0.42077200
B	-7.36310600	0.17077200	0.36704200
H	-7.16616500	-0.72743500	1.16273400
H	-8.54042200	0.39085300	0.21157000
N	-6.69562000	-0.18352000	-1.01419200
H	-6.84173100	0.57409600	-1.68093600
H	-5.67922500	-0.29277300	-0.92871900
B	-7.22138600	-1.51910200	-1.74796100
H	-8.43202000	-1.49848100	-1.76372700
H	-6.73596000	-1.56095000	-2.85889000
N	-6.68987400	-2.73835100	-0.88471700
H	-6.92309000	-2.56389300	0.09348000
H	-7.25012400	-3.54946700	-1.14155200
B	-5.14859000	-3.23066200	-1.01947700
H	-4.86868800	-3.83850000	0.00235300
H	-5.13157300	-3.96412200	-1.99800400
N	-4.18444700	-2.00310200	-1.16924700
H	-3.24998500	-2.40479500	-1.08487200
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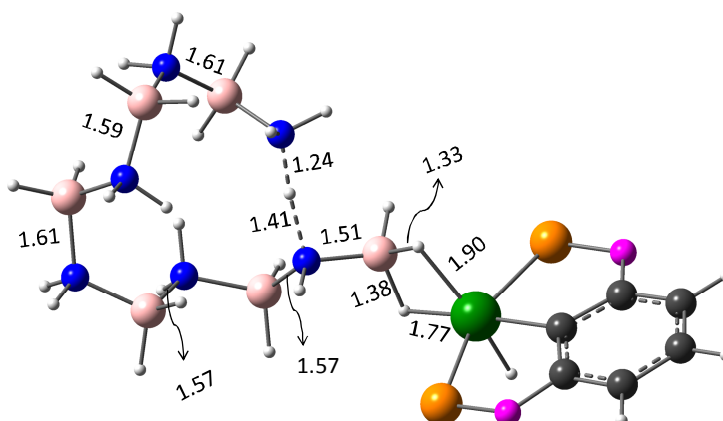
11. *Ts6-6'*



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C	3.33500000	1.75641100	-0.04074000
C	5.18450100	-0.32643300	0.12198200
C	4.69747800	2.06214100	-0.01537900
C	5.61241100	1.00580100	0.06731300
H	5.89386200	-1.14524900	0.18097600
H	5.02967800	3.09392300	-0.06213900
H	6.67632500	1.22389300	0.08727700
P	0.78207100	2.36357200	-0.12982500
P	1.69700300	-2.12556500	0.07595700
C	0.20253200	3.19636800	-1.72910000
C	0.21000900	3.25907000	1.44807600
C	1.57251400	-3.24736200	-1.45172200
C	1.44873400	-3.04898700	1.72193400
O	2.42013800	2.79592000	-0.13178500
O	3.37261100	-1.89757600	0.13879200
H	-1.99624900	-0.65786900	1.77149300
H	-0.84196000	-0.24222900	0.00769400
H	0.60937800	-0.08102700	-1.52768300
B	-2.40390200	-0.35525100	0.69118100
H	-2.66427400	0.74857000	0.35839600
C	-1.26189800	2.79858500	-2.01014900
H	-1.55161600	3.20107800	-2.98871500
H	-1.39475600	1.71409500	-2.03696800
H	-1.95770300	3.20200600	-1.27078600
C	1.10315200	2.64613200	-2.85915800
H	2.15373800	2.90741000	-2.70593200
H	1.02771700	1.55953100	-2.95042700
H	0.77595900	3.08595100	-3.80898800
C	0.34608800	4.73069900	-1.69376800
H	0.10970200	5.12727700	-2.68906400
H	-0.34641300	5.19648600	-0.98807600
H	1.36564400	5.04009200	-1.44552200
C	0.56496900	2.29245100	2.60327900
H	0.01622800	1.34780500	2.51629600
H	1.63815500	2.07977900	2.64669200
H	0.27870700	2.75275900	3.55719900
C	-1.31512000	3.48075600	1.43490500
H	-1.62583000	3.83959400	2.42380000
H	-1.61549100	4.23967700	0.70747500
H	-1.87170300	2.56280300	1.22968600
C	0.94370700	4.59494500	1.68499800
H	0.70607600	5.34588400	0.92925400
H	0.62733300	4.99447300	2.65685500
H	2.02792900	4.46301300	1.70709100
C	1.45482600	-1.94027100	2.80170600
H	2.40300200	-1.39409700	2.82085800
H	0.63725700	-1.22572400	2.65391100

H	1.31622400	-2.39925200	3.78855800
C	0.07900800	-3.75403500	1.74022000
H	-0.09735400	-4.16567000	2.74157200
H	-0.73840500	-3.05823800	1.52623300
H	0.03069400	-4.58700400	1.03301800
C	2.57499500	-4.05003600	2.04831300
H	2.43063500	-4.41544700	3.07303300
H	2.57318100	-4.91962900	1.38927800
H	3.55865600	-3.57783100	1.99263100
C	0.08992300	-3.42796900	-1.83759200
H	0.02938800	-4.03001600	-2.75212900
H	-0.48457500	-3.95483700	-1.06947100
H	-0.39178500	-2.46814500	-2.04379700
C	2.24212500	-4.62122200	-1.25964500
H	1.70050100	-5.25186300	-0.54962300
H	2.24782200	-5.14772300	-2.22212700
H	3.27950500	-4.52578500	-0.92676400
C	2.29674600	-2.50224000	-2.59712300
H	1.87191800	-1.51092600	-2.77547900
H	3.36407400	-2.38674200	-2.39317200
H	2.18544500	-3.08686300	-3.51829700
N	-2.83160000	-1.52947400	-0.24903900
B	-3.48914400	-1.24563700	-1.68733800
H	-3.47305800	-2.27815900	-2.32000800
H	-2.87547000	-0.35165700	-2.22144500
N	-5.00161300	-0.80103100	-1.45553000
H	-5.33280500	-0.45775600	-2.35685900
H	-5.01632500	0.02897600	-0.84570400
B	-5.98437700	-1.92011500	-0.93546600
H	-6.15326000	-2.74002900	-1.80818500
H	-5.53184300	-2.43878800	0.06711600
N	-7.42447900	-1.29486700	-0.54570800
H	-8.03314000	-1.43879400	-1.35143900
H	-7.82228300	-1.91347600	0.16198400
B	-7.74940800	0.23315400	-0.15329500
H	-7.37427600	0.94007700	-1.05949400
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N	-7.04302000	0.71363900	1.18916400
H	-7.45726200	1.63336500	1.34575800
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B	-5.42537300	0.96546900	1.32617600
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H	-5.26950300	1.83128200	2.16801300
N	-4.67336200	-0.31213100	1.73086800
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H	-5.11252600	-1.18951700	1.46525900
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12. Ts7-8

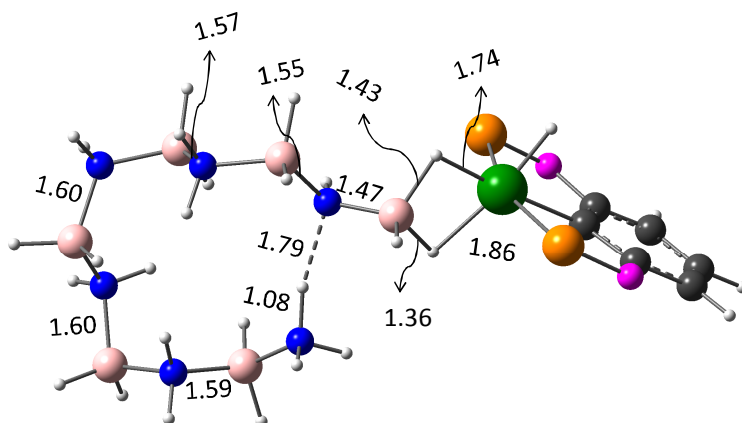


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C	3.63302600	-0.34179900	-1.27634100
C	3.85298700	2.22358500	-2.31472800
C	4.73052200	-0.03011000	-2.08131100
C	4.82477700	1.26181600	-2.60813300
H	3.92752800	3.23838000	-2.69132300
H	5.49065700	-0.77906900	-2.27737000
H	5.66880100	1.52509000	-3.23867100
P	2.22738500	-1.97289000	0.22330500
P	0.64109300	2.39288300	-0.08155500
C	3.03124800	-2.46252400	1.88099700
C	1.63686800	-3.51317100	-0.75758400
C	1.04403900	3.49725000	1.42573900
C	-0.85086200	3.06885200	-1.06733400
O	3.57206100	-1.61201400	-0.71596100
O	1.84491900	2.83022000	-1.16950400
H	-0.47094700	-0.60178100	-0.71294500
H	-0.25729400	-0.29767500	1.38804000
H	2.06766200	0.55759200	1.29997100
B	-1.06322600	-0.88934200	0.44047700
H	-1.03847000	-2.07134300	0.64060100
C	1.91512900	-2.61662800	2.93719200
H	2.37500200	-2.84712700	3.90613100
H	1.33253900	-1.69851500	3.04798800
H	1.22244400	-3.42881600	2.70048900
C	3.97106700	-1.30884000	2.29795900
H	4.77332100	-1.15544700	1.57075100
H	3.43456200	-0.36648900	2.42431700
H	4.42862400	-1.56669300	3.26081900
C	3.87686500	-3.75046700	1.81556600
H	4.37396200	-3.88767400	2.78382300
H	3.27389800	-4.64301800	1.63483700
H	4.65613900	-3.68840200	1.05070600

C	0.86566700	-2.98534600	-1.98925300
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H	0.61657200	-3.83683600	-2.63446700
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H	-0.13412600	-3.86584800	0.50617200
C	2.82715100	-4.34617800	-1.28976200
H	3.40736100	-4.82238700	-0.49959500
H	2.42125200	-5.14494500	-1.92317200
H	3.50313800	-3.74197700	-1.89780000
C	-1.17433700	2.01444200	-2.15064900
H	-0.31062600	1.82245700	-2.79492800
H	-1.49302300	1.06021400	-1.73026100
H	-1.98448500	2.39848700	-2.78260600
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H	-2.96586900	3.42380300	-0.76449000
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C	-0.52190700	4.38613300	-1.80736600
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H	-0.33231000	5.22140800	-1.13394900
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H	0.45616000	3.61612400	3.50406400
H	-0.88167000	3.14498000	2.44973600
H	0.37131500	1.96915000	2.85256200
C	0.81796900	5.00308600	1.18332900
H	-0.23452400	5.25472100	1.03761800
H	1.16123100	5.55051900	2.06990400
H	1.39248500	5.36926800	0.32774500
C	2.54187300	3.30451000	1.75468700
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H	2.77871800	3.90200300	2.64341700
N	-2.47108300	-0.35976000	0.50212400
H	-3.14851200	-1.25899200	-0.34155000
H	-2.54644700	0.56398800	0.08282600
B	-3.02040100	-0.28813700	1.97202300
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H	-4.91052400	-0.29332500	2.94244600
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B	-5.28878000	1.12270500	1.38023400
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N	-6.87527700	0.90813300	1.15462100
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H	-7.25344000	-1.30705000	0.75007900
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N	-6.53821000	-0.21206900	-1.14439700
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B	-6.54263900	-1.45618200	-2.14097900
H	-7.64888100	-1.57585100	-2.61348300
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N	-6.16350000	-2.78924600	-1.35502400
H	-6.92572100	-3.00121800	-0.71051900
H	-6.20419900	-3.52779600	-2.05681800
B	-4.80672200	-2.96959200	-0.50071100
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13. 8

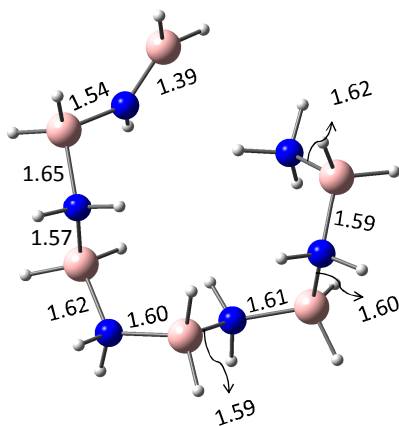


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C	-3.32438000	2.34393400	2.68906300
C	-4.38571100	0.16372700	2.53802300
C	-4.31128900	1.44219400	3.10005100
H	-3.27005700	3.34875900	3.09488700
H	-5.16223400	-0.53758800	2.82527700
H	-5.03606700	1.74282000	3.85082800
P	-2.43144300	-1.83986400	-0.20250400
P	-0.45079500	2.35588300	0.02760200
C	-3.54865400	-2.08427400	-1.73341500
C	-1.86995800	-3.52703600	0.52048700
C	-0.99043300	3.52821700	-1.38593500

C	1.20471900	2.92063500	0.79740600
O	-3.54775500	-1.45249500	0.99066200
O	-1.45816900	2.84449100	1.28250400
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H	-3.86409000	0.08464400	-1.96439000
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C	-4.48295700	-3.30901200	-1.65822500
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C	2.28972500	3.06480200	-0.28918300
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H	2.33026100	2.21510800	-0.97563100
H	2.14599500	3.96586200	-0.89117800
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H	2.03364600	4.43104400	2.09061400
H	0.86591200	5.10473900	0.95599000
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C	-0.35223300	3.03648700	-2.70301600
H	-0.71513000	3.66184300	-3.52829600
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C	-0.63188300	5.00940000	-1.14926000
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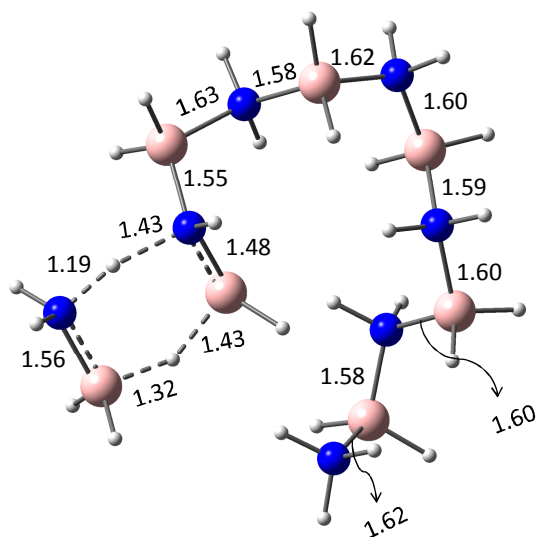
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N	2.33398500	-0.62859100	-0.85861300
H	2.33339700	-1.82383800	2.01708100
H	2.48828900	0.34514700	-0.61424700
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H	2.66530400	-0.13358200	-3.09681600
H	2.73654500	-2.08189300	-2.57318700
N	4.61384000	-0.83696200	-2.14959900
H	4.90382200	-1.02880300	-3.10957900
H	4.96090500	-1.63058700	-1.61108600
B	5.29691800	0.48600500	-1.64599700
H	5.08208300	1.38370500	-2.42782700
H	4.92762000	0.74918700	-0.52134600
N	6.89390400	0.23746600	-1.57480600
H	7.24025300	-0.00024600	-2.50594300
H	7.32722000	1.14233000	-1.38265700
B	7.46906300	-0.86566200	-0.56790700
H	6.88292500	-1.90898500	-0.79394100
H	8.66056500	-0.98669800	-0.72617600
N	7.18356200	-0.40459200	0.92280600
H	7.90720300	0.24522500	1.22725200
H	6.30322900	0.11568100	0.98451500
B	7.13752600	-1.57203100	2.01775000
H	8.05450300	-2.33362000	1.82404700
H	7.12311100	-1.09787000	3.12747000
N	5.74554900	-2.33735000	1.75822300
H	5.72083600	-2.52710300	0.75315200
H	5.83104000	-3.25022500	2.20288900
B	4.45724900	-1.58868400	2.30139300
H	4.29280100	-1.89640200	3.45625500
H	4.55532800	-0.39811900	2.13436700
N	3.15893900	-2.05287500	1.46182000
H	2.99116600	-1.54406600	0.52571000
H	3.10042100	-3.05818000	1.29202700

14. 9



H	-1.85930600	3.45743100	-0.93838800
B	-2.30423000	2.68061900	-0.12330500
H	-2.61859200	3.07425400	0.96267500
N	-2.38019200	1.32447200	-0.44012400
H	-2.18669100	1.08445300	-1.40871200
B	-3.11110200	0.21425300	0.34187400
H	-3.99235000	-0.29565700	-0.31840900
H	-3.49218400	0.63111600	1.41474700
N	-2.06089400	-1.00744800	0.68240300
H	-2.58814700	-1.61564300	1.30963900
H	-1.31332500	-0.61254000	1.25527100
B	-1.49478900	-1.83656200	-0.52162100
H	-2.35531200	-2.55051100	-0.97490600
H	-1.03794100	-1.08956400	-1.36912500
N	-0.27749800	-2.77165900	-0.00099700
H	-0.60986200	-3.35414400	0.76949700
H	-0.08503200	-3.44560700	-0.74412800
B	1.08147300	-2.08454500	0.47766100
H	0.79997400	-1.34228100	1.39990400
H	1.89409500	-2.91801800	0.79736200
N	1.64106200	-1.23254000	-0.74218700
H	1.98992700	-1.87396600	-1.45573800
H	0.83971200	-0.77474400	-1.18445100
B	2.86341500	-0.21527200	-0.51655000
H	3.85839800	-0.87115000	-0.33296700
H	2.95281500	0.49818300	-1.49645900
N	2.57214900	0.68124300	0.78085700
H	1.99315600	0.13321800	1.42141300
H	3.46432200	0.77300900	1.26498600
B	2.02593700	2.16714900	0.65181200
H	1.51124900	2.52771300	1.67978000
H	2.91666000	2.88086100	0.26515000
N	0.89344000	2.19815500	-0.49926100
H	0.61405200	3.16647500	-0.66359400
H	1.27123400	1.83740900	-1.37837800
H	0.01315400	1.70593000	-0.28935600

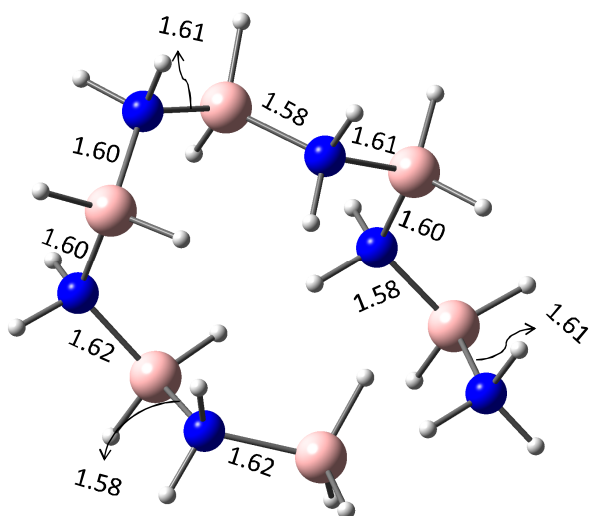
15. Ts9-10



H	-0.76337000	0.85936600	-1.12467300
B	-1.33704900	0.29788000	-0.21568800
H	-0.85065500	0.45425100	0.88585800
N	-1.91855800	-1.03229900	-0.50108500
H	-3.29454400	-0.67320600	-0.33246500
B	-1.75073900	-2.24709100	0.45157200
H	-2.19035000	-3.26146400	-0.04900800
H	-2.26389500	-2.00052000	1.53246900
N	-0.16852200	-2.50252500	0.76374000
H	-0.14537400	-3.22615300	1.48227700
H	0.17115000	-1.65671300	1.22514100
B	0.77711800	-2.90175900	-0.43215800
H	0.68598800	-4.08793400	-0.64981100
H	0.52712400	-2.23634900	-1.41425200
N	2.30941100	-2.57441200	-0.02237000
H	2.58391200	-3.16423500	0.76501300
H	2.88661000	-2.91633400	-0.79235600
B	2.74324700	-1.07975600	0.35682500
H	2.13802200	-0.76782000	1.36188400
H	3.94118200	-1.02780000	0.51243500
N	2.32650100	-0.11097400	-0.82921400
H	2.88872800	-0.32631100	-1.65362400
H	1.36503300	-0.31553000	-1.11464900
B	2.48875900	1.46780600	-0.61724900
H	3.65661100	1.74438900	-0.51330300
H	1.96914000	2.01628100	-1.57347500
N	1.72567400	1.88787100	0.71917200
H	0.93553900	1.25935200	0.89272600
H	2.35128500	1.73024800	1.50845800
B	1.21107300	3.37825900	0.82106900
H	0.66714900	3.57864400	1.87918200
H	2.09068900	4.15626400	0.55578500

N	0.07815000	3.52745800	-0.33334400
H	-0.26258000	4.48703500	-0.36572300
H	0.48115100	3.29033800	-1.24365900
H	-0.72674900	2.91062200	-0.19509800
H	-1.81251800	-1.29902200	-1.47600000
H	-2.39340600	1.25163400	-0.05568200
B	-3.69931300	1.41373300	0.00382800
H	-3.86485400	1.94298900	1.07110100
H	-3.95144000	2.06389000	-0.97949100
N	-4.26407600	-0.03473100	-0.07909000
H	-4.64027100	-0.38644800	0.79799000
H	-4.96485800	-0.16754400	-0.80271300

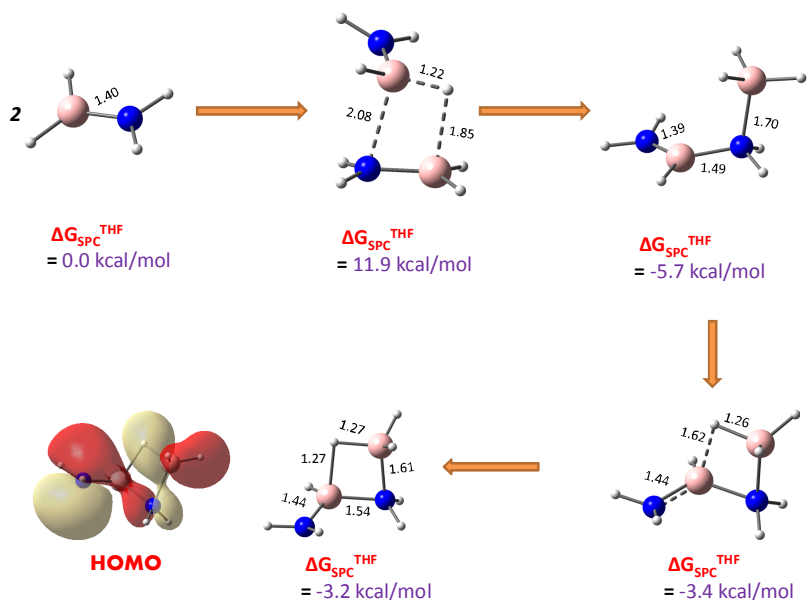
16. 10



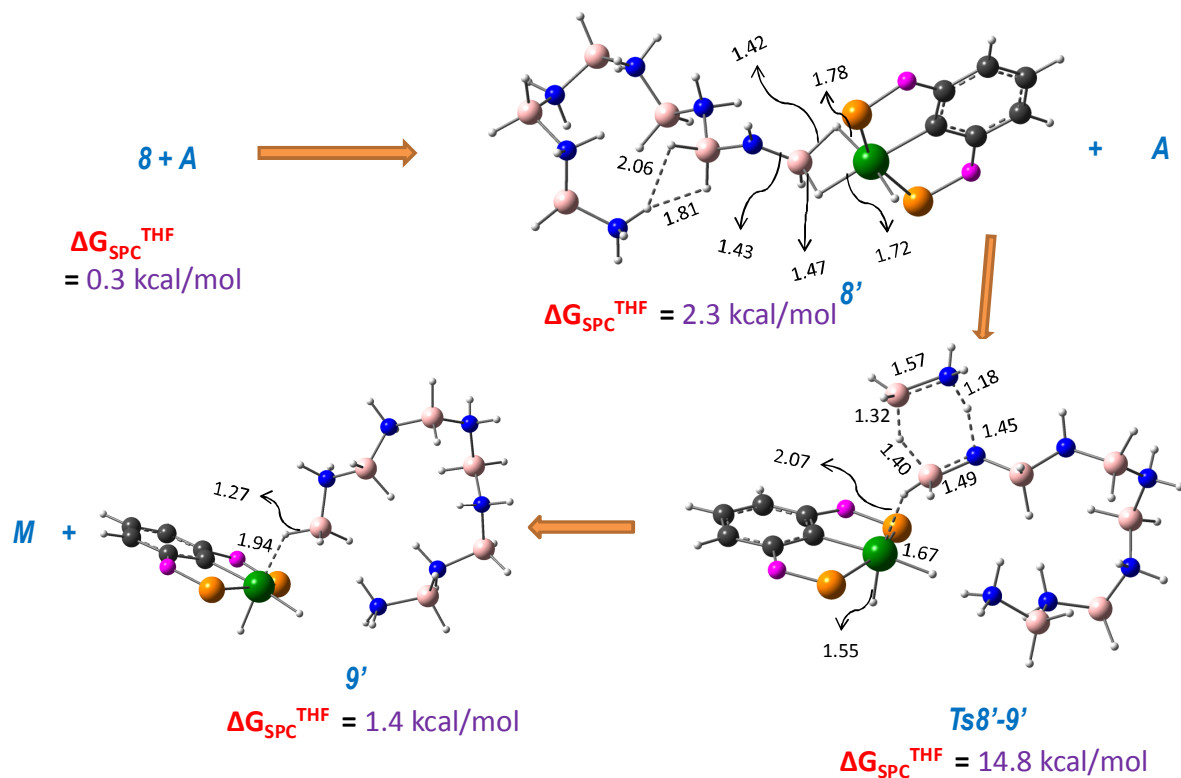
H	0.77598000	2.94999200	-0.59210100
B	0.03344700	2.04452800	-0.22375300
H	0.20172500	1.83036300	0.96701300
N	-1.49077300	2.45579400	-0.49037500
H	-1.56945400	3.46956100	-0.42834700
B	-2.63830500	1.89935100	0.47022700
H	-3.72014500	2.05344400	-0.04921000
H	-2.53252300	2.46730700	1.53537100
N	-2.39656900	0.33545600	0.71881600
H	-3.02668500	0.09416200	1.48398500
H	-1.45715000	0.23428300	1.10910900
B	-2.61736300	-0.66560800	-0.48280200
H	-3.80054100	-0.77562400	-0.70346300
H	-1.99883700	-0.29094900	-1.45545600
N	-2.03773500	-2.11342100	-0.06157200
H	-2.60709600	-2.49502300	0.69578400
H	-2.23534800	-2.73711800	-0.84595900
B	-0.50775000	-2.28814500	0.39485300
H	-0.34715600	-1.61338700	1.39057600

H	-0.27840300	-3.45805000	0.59532600
N	0.42640900	-1.75528400	-0.76685300
H	0.38804700	-2.39898100	-1.55779300
H	0.05304400	-0.86991700	-1.12213900
B	1.98774000	-1.54334600	-0.47279700
H	2.50257000	-2.60202900	-0.21573900
H	2.46918700	-1.02851600	-1.46745200
N	2.14601300	-0.55555800	0.77064000
H	1.32281700	0.04737500	0.86196300
H	2.15463600	-1.10939400	1.62584100
B	3.42601400	0.37243000	0.79381700
H	3.45445600	1.04498000	1.79557700
H	4.42686200	-0.26825600	0.59593200
N	3.24332900	1.38496500	-0.45949200
H	4.05294600	1.99902300	-0.52923400
H	3.16838100	0.84653200	-1.32594900
H	2.39994700	1.97276100	-0.39724400
H	-1.72078200	2.23075800	-1.45756700
H	0.26988800	1.04698000	-0.88469300

S4. Formation of In situ Nucleophile in case of solvent assisted Oligomerization of amino-borane (M) :



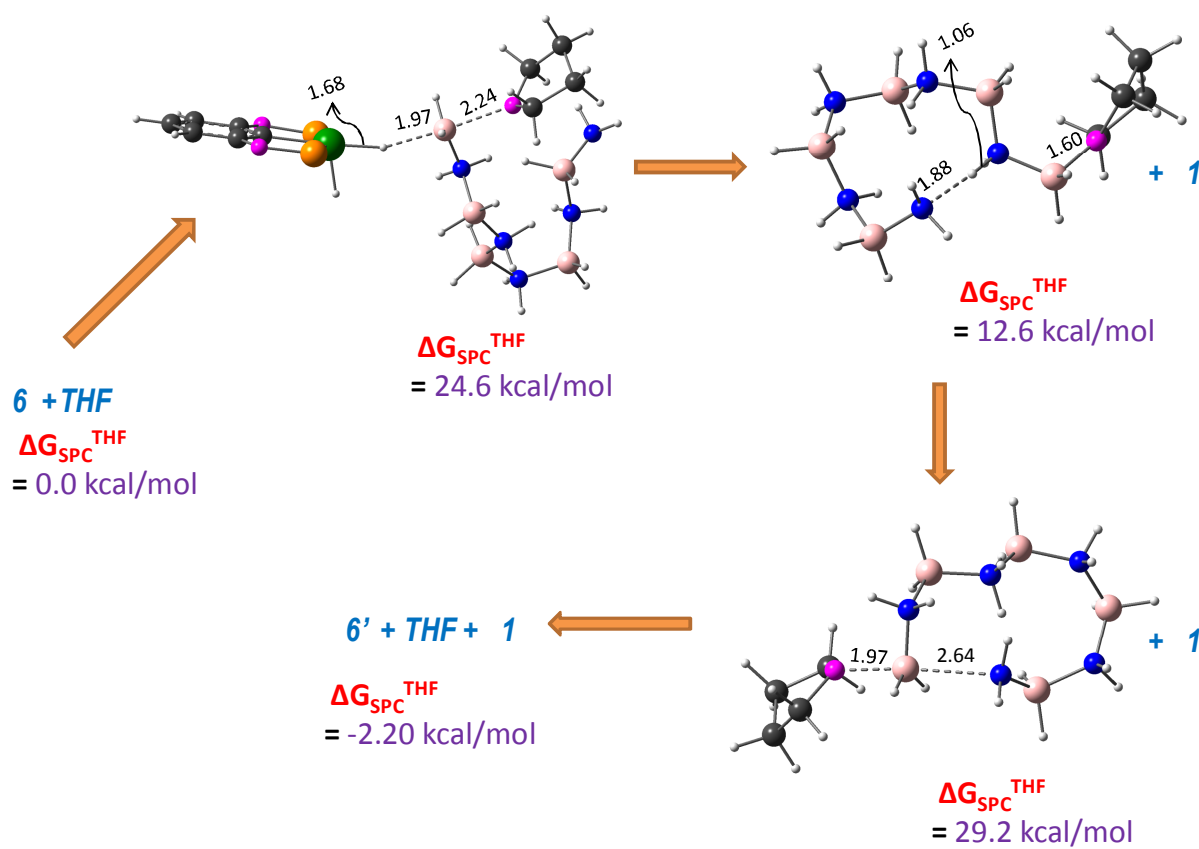
S5. Another possible pathway for chain termination of Polyaminoborane:



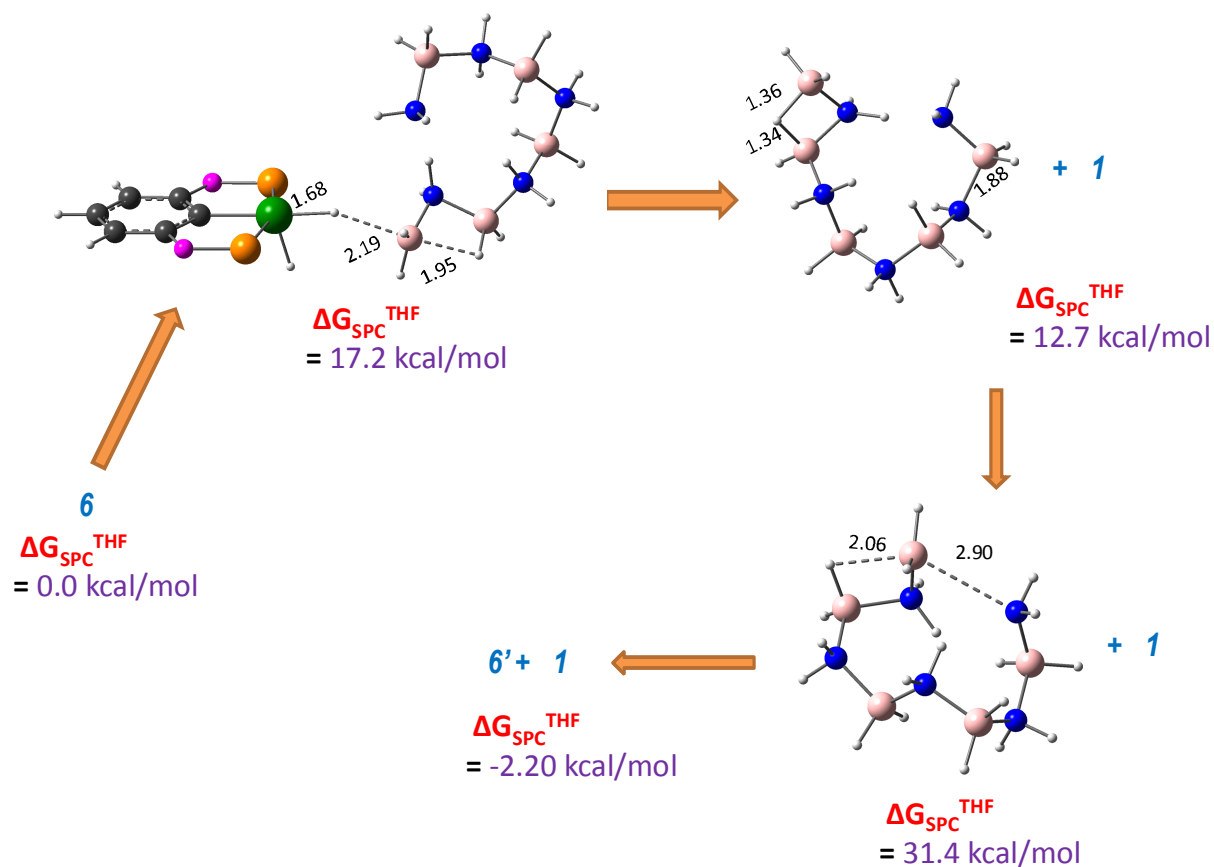
This pathway of chain termination may not be operative as it has a slightly higher free energy barrier compared to our reported pathway in the manuscript.

S6. Possible pathways leading to formation of Cyclic Pentamer $(\text{NH}_2\text{BH}_2)_5$:

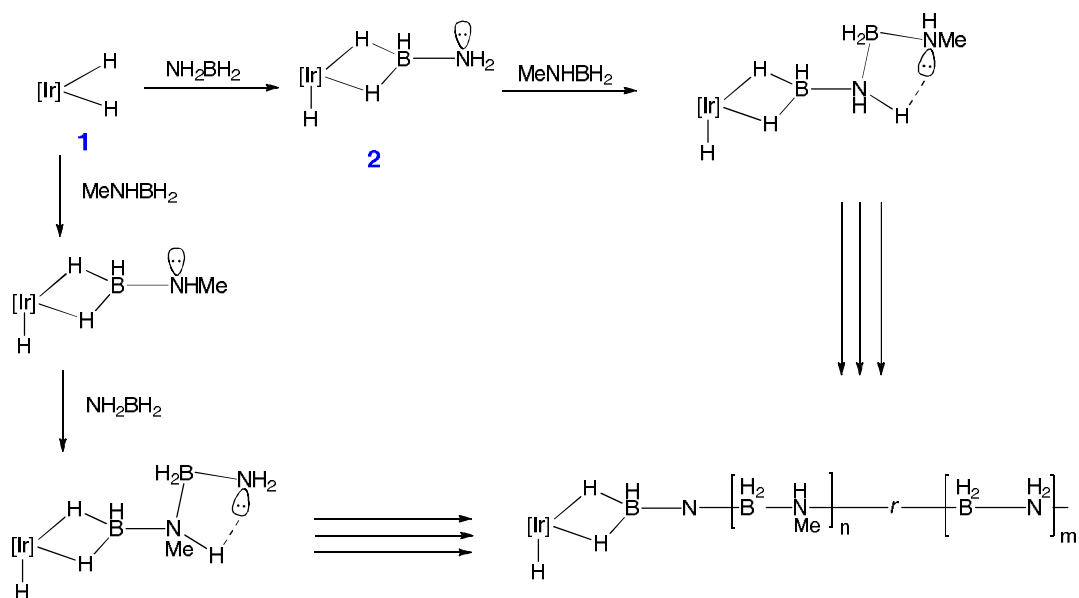
1. In assistance of THF:



2. In assistance of B-H bond through a 4-member ring:

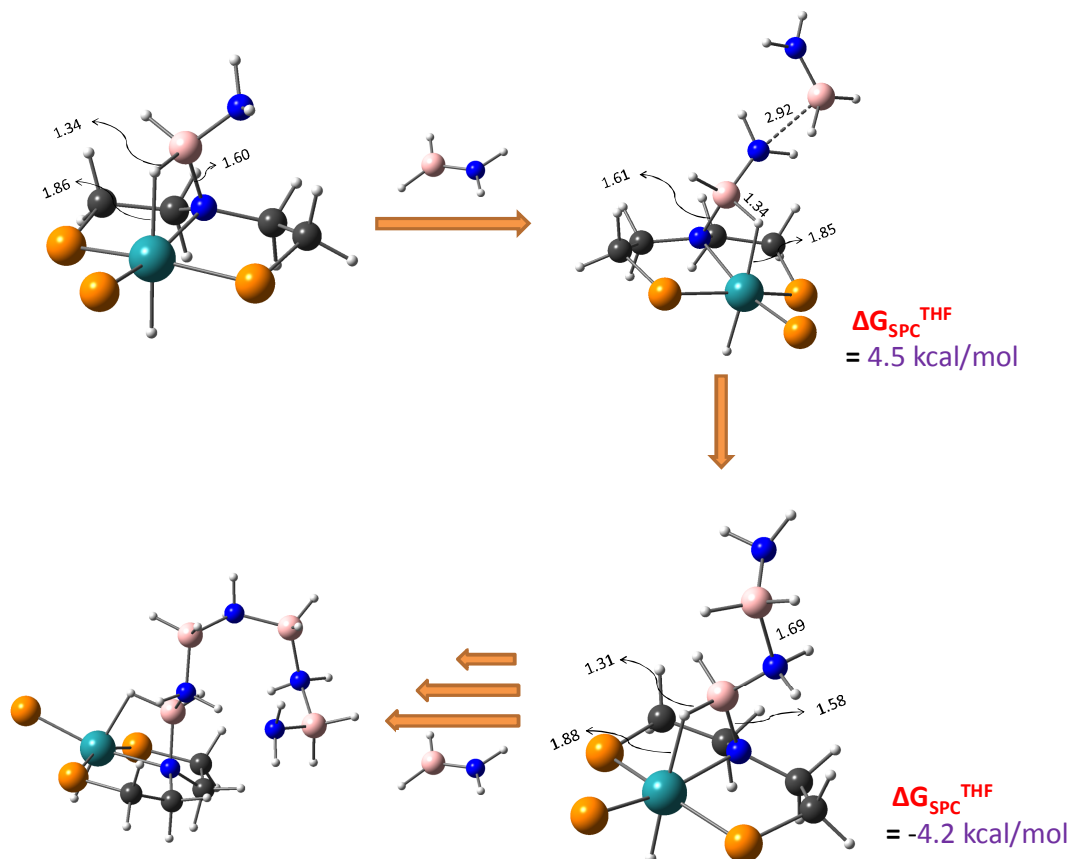


S7. Formation of copolymer of NH_3BH_3 and NMeH_2BH_3 in presence of IrH_2POCOP :



S8. Formation of Polyaminoborane of NH_3BH_3 in presence of $\text{RuH}(\text{PMe}_3)(\text{PNP})$:

Note: Methyl groups on P atoms are omitted for clarity.

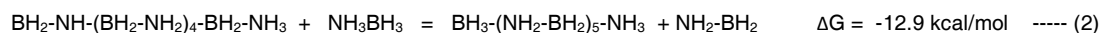


S9. Ammonia-borane dehydrogenation and aminoborane oligomerization are separate event at Ir centre :

We are of the opinion that the dehydrogenation of ammonia-borane and the oligo-polymerization processes which occur separately at the Ir catalyst. This view is consistent with the inferences drawn by Manners and co-workers based on their extensive kinetic studies on the dehydropolymerization process using the Ir -pincer catalyst (*J. Am. Chem. Soc.* **2010**, *132*, 13332–13345). In the reaction medium it is expected that initially the dehydrogenation reaction would dominate due to large presence of ammonia-borane. This rate would fall off with progress of time as ammonia-borane gets depleted from the reaction medium. As ammonia-borane is being dehydrogenated at most of the IrH_2 centres we believe a small fraction of the IrH_2 centres would preferentially bind NH_2BH_2 over NH_3BH_3 . These would immediately initiate the polymerization process as delineated by us in the report by adding up NH_2BH_2 units rapidly as they are produced from other catalytic centres. The binding of NH_2BH_2 to the IrH_2 species is thermodynamically more favorable compared to that of ammonia-borane. These NH_2BH_2 bound metallic species quickly start chain propagation of polyaminoborane formation through low barrier channels as discussed in our report. Concomitantly dehydrogenation of ammonia-borane would occur at other IrH_2 centres producing more NH_2BH_2 in the process, which in turn would help the polymer formation. The polymerization rate would pick up as more and more NH_2BH_2 are produced. Additionally the oligo-polymerization route unraveled by us has really paltry chain initiation, chain propagation and chain termination barriers. So the rate of polyaminoborane formation is very fast, which ensures rapid polyaminoborane formation and also freeing up of the metal centre for further dehydrogenation of ammonia-borane. When amino-borane concentration falls due to rapid depletion of aminoborane from the system, again dehydrogenation process would dominate producing aminoborane which would again favorably bind to some metal catalyst molecules and facilitates further polymer assembly. So both the processes occur side by side and rate depends on the relative concentration of ammonia-borane and aminoborane in the reaction medium. We admit that this is a conjecture because

quantum chemical studies would only predict barriers and binding energies, but the ultimate proper treatment would require an explanation based on statistical mechanics and diffusivity which we believe is anything but trivial and beyond the scope of the current work. However we would like to assert that our conjecture is well supported by the experimental findings of Manners et al. and also the evidence provided through low reaction barriers and binding energies as found from our quantum chemical study. Our proposed mechanism study shows for the first time how the oligomerization can occur rapidly at the transition metal centre and the overall barriers of the process suggest that this process is so rapid that it would not hamper ammonia-borane dehydrogenation. We provide some crucial free energy changes for formation of $\text{Ir}(\text{H})_2$ species from $\text{Ir}(\text{M})_n$ below. We have shown in our report that after aggregation of **M** at the metal centre, dissociation of oligomer from metal centre is slightly endothermic (9.6 kcal/mol) to regenerate active catalyst which can dehydrogenate amine-borane to produce further amino-borane. But the subsequent process makes the regeneration of $\text{Ir}(\text{H})_2$ an exothermic process.

For $n=6$, thermodynamics of the regeneration pathway is shown below



As a result of (1) and (2) we get that formation of $\text{Ir}(\text{H})_2$ from $\text{Ir}(\text{M})_n$ is exothermic by -3.3 kcal



S10. Free NH_2BH_2 is produced in solution:

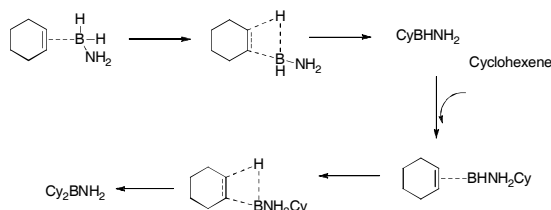
Baker and co-workers had devised an elegant way of trapping NH_2BH_2 using cyclohexene (*Chem. Commun.*, **2008**, 6597-6599). This trapping experiment has been used to infer whether free NH_2BH_2 is being produced during ammonia-borane dehydrogenation by different agents. In case of ammonia-borane dehydrogenation by the Brookhart's Ir-pincer catalyst, NH_2BH_2 is not trapped by using cyclohexene at room temperature (*J. Am. Chem. Soc.* 2010, 132, 13332–13345; *Chem. Commun.*, 2008, 6597-6599). However, Baker and co-workers reported that if the reaction temperature is elevated to 60°C then some hydroboration product is obtained (*Chem. Commun.*, **2008**, 6597-6599). There can be two plausible explanations for these experimental findings:

(a) the obvious reason being that free NH_2BH_2 is not produced at room temperature.

(b) There can be a subtle alternative explanation for this experimental observation. A trapping agent can effectively trap an intermediate if the reaction responsible for trapping the intermediate has a faster or comparable rate compared to any side reaction which consumes the targeted intermediate from reaction medium. If the reaction rate for hydroboration of cyclohexene by NH_2BH_2 is much slower compared to polymerization of NH_2BH_2 , cyclohexene would not be able to trap NH_2BH_2 . This can only happen at a much higher activation barrier for hydroboration as compared to oligo-polymerization of NH_2BH_2 by the Ir catalyst. Furthermore at slightly elevated temperatures one can expect a small amount of hydroboration product as the higher barrier trapping reaction is then expected to yield some product.

We have proposed an oligomerization pathway which involves free NH_2BH_2 , clearly subscribing to the view put forward by Baker et al that no free NH_2BH_2 is released during Ir-pincer catalyzed ammonia-borane dehydrogenation. Intriguingly almost all theoretical studies on Transition metal species catalyzed dehydrogenation of ammonia-borane predict the formation of free NH_2BH_2 (*J. Am. Chem. Soc.* **2008**, 130, 1798-1799, *J. Am. Chem. Soc.* **2013**, 135, 13342–13355). This stark difference between the experimentalists and theoreticians perception can only be reconciled through the explanation provided in (b).

It turns out that the direct hydroboration of cyclohexene by NH_2BH_2 and producing $\text{NH}_2\text{B}(\text{Cy})_2$ has a rate determining barrier of 27 kcal/mol. As soon as we compare this barrier to the polymerization steps (chain initiation barrier: 3.3 kcal/mol chain propagation: 5-7 kcal/mol). Comparison of these barriers would immediately suggest that the trapping agent would fail to trap aminoborane as the oligomerization of aminoborane is much faster. However, one may expect a small amount of hydroboration at elevated temperatures as was found by Baker et al (*Chem. Commun.*, **2008**, 6597-6599).



Experimental evidence in favor of our mechanism:

As mentioned earlier there are two schools of thought regarding polyaminoborane formation. While Baker and co-workers based on their trapping experiments inferred that NH_2BH_2 is not released in the medium from the Ir catalyst a contrasting view was presented by Manners and co-workers based on their experiments on Polyaminoborane formation by the same Ir catalyst. Recently Manners and coworkers reported based on their experimental finding that the appropriate hypothesis for IrH_2POCOP catalyzed ammonia-borane dehydrogenation would be -

- (i) IrH_2POCOP dehydrogenates ammonia-borane (NH_3BH_3) to produce aminoborane (NH_2BH_2).
- (ii) The insitu generated amino-borane (NH_2BH_2) then oligomerizes in presence of IrH_2POCOP catalyst.