

Acidity enhancement of unsaturated bases of the group 15 by association with borane and beryllium dihydride. Unexpected boron and beryllium Brønsted acids.

Ana Martín-Sómer, Otilia Mó, Manuel Yáñez and Jean-Claude Guillemin

Contribution from Departamento de Química, Facultad de Ciencias, Módulo 13, Universidad Autónoma de Madrid, Campus de Excelencia UAM-CSIC, Cantoblanco, 28049 Madrid (Spain) and Institut des Sciences Chimiques de Rennes, École Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France.

Supporting Information
(A total of 23 pages)

Table S1. Optimized geometries (Å) of the complexes formed upon interaction of $\text{CH}_3\text{-CH}_2\text{XH}_2$, $\text{CH}_2=\text{CHXH}_2$, $\text{HC}\equiv\text{CXH}_2$ (X = N, P, As, Sb) with BeH_2 and BH_3

Ethylamine: BeH_2

C	-1.45019600	0.57775700	-0.21308500
H	-1.58051900	0.46136400	-1.29581900
H	-2.44539400	0.58859500	0.24145000
C	-0.61903800	-0.55636900	0.37371900
H	-0.48786600	-0.41280200	1.44904100
N	0.74881700	-0.56763700	-0.22328200
H	1.25969100	-1.39988700	0.07969700
H	0.69552300	-0.64994400	-1.23987100
Be	1.86063800	0.75959300	0.15833400
H	1.46272700	1.46907900	1.25624700
H	2.91239300	0.73002100	-0.71603700
H	-1.11173900	-1.52274800	0.20880800
H	-0.97368300	1.54307500	-0.01768100

Deprotonated Ethylamine: BeH_2

C	-1.64605300	0.03250800	-0.44016800
H	-1.87035400	-1.02563100	-0.63592900
H	-2.56841600	0.51173000	-0.07206900
C	-0.48645800	0.16716500	0.57231500
H	-0.29949600	1.23663600	0.73918600
N	0.75420900	-0.43100500	0.14985100
H	0.68205300	-1.44444200	0.11346000
Be	2.11067100	0.28138100	-0.29473600
H	2.15322200	1.70868800	-0.23841300
H	3.19261100	-0.54792300	-0.71620200
H	-0.85197800	-0.23842000	1.54178700
H	-1.36472600	0.49283000	-1.39470900

Ethylphosphine: BeH_2

C	2.21118300	-0.08094500	0.00001100
H	2.31356000	-0.71771700	-0.88496100
H	3.04727700	0.62687900	-0.00002300
C	0.87468100	0.66830500	-0.00003000
H	0.78762200	1.32315000	0.87463000
Be	-2.74135200	0.46688500	0.00000300
H	-2.70131200	1.82312800	0.00010800
H	-3.58860700	-0.59439700	-0.00013300
H	0.78762100	1.32305600	-0.87476100
H	2.31355400	-0.71762800	0.88504800
P	-0.64980600	-0.39213700	0.00000500

H	-0.38116200	-1.28810900	-1.06271500
H	-0.38124000	-1.28800600	1.06283000

Deprotonated Ethylphosphine:BeH₂

C	-2.17011700	-0.01629800	-0.00852900
H	-2.31466800	-0.78807500	0.75847600
H	-2.97951300	0.72289200	0.10654400
C	-0.78048300	0.62587200	0.11164900
H	-0.66318100	1.40455300	-0.65275300
Be	2.48643700	0.57512300	0.05847600
H	2.44523800	1.90381400	-0.39028300
H	3.61439800	-0.10350900	0.53391800
H	-0.69535300	1.13759900	1.07967600
H	-2.28882200	-0.50645400	-0.98246600
P	0.67230400	-0.56248900	-0.15830100
H	0.55519200	-1.29141800	1.06878100

Ethylarsine:BeH₂

C	2.48621300	-0.07375500	0.00001400
H	2.54514800	-0.71649900	-0.88453000
H	3.37134500	0.57286600	0.00001100
C	1.20944800	0.76830900	-0.00000700
H	1.16666400	1.42432400	0.87640200
Be	-2.64674900	0.63256500	-0.00002200
H	-2.63808500	1.98601300	-0.00017500
H	-3.44094000	-0.46640900	0.00013000
H	1.16667300	1.42429400	-0.87643800
H	2.54513600	-0.71647300	0.88457800
H	-0.20915600	-1.21961100	-1.10785400
H	-0.20916000	-1.21959400	1.10787200
As	-0.48135100	-0.23534800	0.00000100

Deprotonated Ethylarsine:BeH₂

C	-2.45514200	0.04332200	0.03533000
H	-2.54995700	-0.64149000	0.88777600
H	-3.30805200	0.74106400	0.07399500
C	-1.10934100	0.77511500	0.06191900
H	-1.03820900	1.46233500	-0.79052600
Be	2.24899800	0.99218600	0.10261700
H	2.09492300	2.27398700	-0.44157100
H	3.41746600	0.46116000	0.65610400
H	-1.04060900	1.39803800	0.96180900
H	-2.55432300	-0.56327700	-0.87338100
H	0.44034100	-0.95859800	1.33108300
As	0.51301000	-0.39553300	-0.08482600

Ethylstibine:BeH₂

C	2.73796900	0.08953900	0.05921400
H	2.76869800	-0.34983900	1.05758300
H	3.61676100	0.73224100	-0.04606700
H	2.83598700	-0.72269100	-0.66301900
C	1.46021600	0.89055500	-0.16318600
H	1.36333700	1.70461600	0.55656800
H	1.43605300	1.33885900	-1.15772500
Sb	-0.39263700	-0.24615300	0.00678700
H	0.00244100	-1.05368900	1.45729500
H	0.07062600	-1.55126200	-0.99235400
Be	-2.78464300	1.04077700	0.00573900
H	-3.62659300	0.31822200	-0.75163800
H	-2.49335200	2.09369400	0.79411100

Deprotonated Ethylstibine:BeH₂

C	-2.71906800	0.10807300	0.05894900
H	-2.80577300	-0.55650900	-0.80502900
H	-3.60171400	0.76411600	0.06520200
H	-2.77540200	-0.52269100	0.95046200
C	-1.41290300	0.89569400	0.02103300
H	-1.36429600	1.52589100	-0.87008300
H	-1.33365900	1.56011700	0.88247600
Sb	0.43503300	-0.33836200	-0.05880700
H	0.31069800	-0.82903100	1.59543700
Be	2.21243600	1.41127400	0.12014200
H	1.92388400	2.61965700	-0.50110800
H	3.40163700	1.02719600	0.72135900

Vinylamine:BeH₂

C	-1.64726500	-0.21289400	-0.30426000
H	-1.70790600	-1.29711400	-0.26216800
H	-2.49269800	0.31912500	-0.72443700
C	-0.57828800	0.45929600	0.11930800
H	-0.49837400	1.53897600	0.05130900
N	0.62544800	-0.16560900	0.60673700
H	0.96832900	0.31093300	1.44119000
H	0.47511500	-1.14765000	0.83064300
Be	1.92590800	-0.02060900	-0.64429600
H	2.21513600	1.29734300	-0.83604000
H	2.31194900	-1.25832900	-1.06075900

Deprotonated (N) Vinylamine:BeH₂

C	1.81745400	-0.07447600	0.00031800
H	2.07524200	-1.13299200	0.00096400
H	2.63502500	0.63974400	0.00030300
C	0.52039500	0.35475400	-0.00035000
H	0.33756800	1.43177200	-0.00080700
N	-0.63188700	-0.37038800	-0.00041100
H	-0.45142800	-1.37150200	-0.00018200
Be	-2.16615000	0.15606100	0.00026300
H	-3.17511100	-0.83544600	0.00051900
H	-2.36058200	1.55522400	0.00121900

Deprotonated (Be) Vinylamine:BeH₂

C	-2.07497800	0.08128200	0.00064600
H	-2.29700400	1.15203900	0.00167600
H	-2.96133000	-0.56773100	0.00061100
C	-0.79855500	-0.36216300	-0.00074200
H	-0.73837400	-1.46766500	-0.00204700
Be	0.68861000	0.61342600	-0.00072800
H	0.66457600	2.03904800	-0.00137000
N	2.08779400	-0.15162300	0.00010700
H	2.20773100	-1.15925700	0.00203900
H	2.99659500	0.29650400	0.00182900

Vinylphosphine:BeH₂

C	2.12903100	0.13321100	0.33240800
H	2.24017100	-0.77660100	0.91719100
H	3.00183200	0.77726300	0.26473000
C	0.98416400	0.46088200	-0.27491600
H	0.90464300	1.39014700	-0.83631600
P	-0.57724700	-0.47069800	-0.14415600
H	-0.72240100	-0.99709700	-1.45163600
H	-0.14385500	-1.64914200	0.50764900
Be	-2.43678100	0.71465300	0.38578800
H	-2.27877900	1.86413500	-0.32260800
H	-3.27495200	0.02860000	1.19522900

Deprotonated (P) Vinylphosphine:BeH₂

C	2.11849000	0.13320800	0.31314400
H	2.28452000	-0.75717200	0.91765900
H	2.96743700	0.80480300	0.19206800
C	0.91862900	0.40210400	-0.24979400
H	0.84036400	1.32313600	-0.83384800
P	-0.63179700	-0.53706300	-0.26111000

H	-0.31461900	-1.50706100	0.73711600
Be	-2.25804200	0.71690600	0.38039800
H	-3.27620500	0.08350100	1.08993700
H	-2.21508700	2.02923500	-0.08798100

Deprotonated (Be) Vinylphosphine:BeH₂

C	-2.73670400	0.01761100	0.03598600
H	-3.01502400	1.07235500	0.09457400
H	-3.58259200	-0.68162200	0.04289900
C	-1.44091100	-0.35715900	-0.03646100
H	-1.31263700	-1.45092200	-0.09064600
Be	-0.07186500	0.74166200	-0.00556200
H	-0.19859800	2.13455100	-0.02926500
P	1.92770400	-0.09639000	-0.10380200
H	1.87128300	-1.24985000	0.74126300
H	2.67515300	0.69198400	0.82331400

Vinylarsine:BeH₂

C	2.43239100	0.14662600	0.34858400
H	2.46359700	-0.72917500	0.99226500
H	3.36366300	0.69589700	0.23291300
C	1.31943700	0.53993600	-0.27398000
H	1.33315800	1.43240400	-0.89697300
H	-0.57436900	-0.91943000	-1.42529500
H	-0.04264300	-1.51529300	0.66659200
Be	-2.41472500	0.87278100	0.40577700
H	-2.27477000	2.17088100	0.05224700
H	-3.26558700	-0.08270200	0.84798000
As	-0.41985200	-0.26251700	-0.07698400

Deprotonated (As) Vinylarsine:BeH₂

C	2.39273700	0.27055500	0.33625500
H	2.48572800	-0.40918600	1.18200300
H	3.29095600	0.82090900	0.05621700
C	1.22949400	0.43284500	-0.32429200
H	1.23266800	1.14396200	-1.15486400
H	-0.19382100	-1.07802400	1.21763100
Be	-1.93394600	1.25363700	0.35035700
H	-2.95251700	0.92239200	1.23991100
H	-1.78545400	2.41861300	-0.39826000
As	-0.48712600	-0.39556400	-0.10957100

Deprotonated (Be) Vinylarsine:BeH₂

C	-3.40776800	0.01446200	0.01715900
H	-3.68020800	1.07178300	0.04474200

H	-4.25772000	-0.68001200	0.01768800
C	-2.11247400	-0.36688000	-0.01309600
H	-1.98383100	-1.46119300	-0.03877500
Be	-0.76333700	0.74770600	0.02662200
H	-0.92628400	2.13591200	-0.01188500
As	1.32655800	-0.04520800	-0.06075700
H	1.25085500	-1.25720300	0.85744900
H	1.99558500	0.80626100	1.00489600

Vinylstibine:BeH₂

C	2.40308100	0.89377200	-0.00001600
H	1.90129500	1.85530600	0.00016700
H	3.48858700	0.92032300	-0.00010500
C	1.74110200	-0.25671300	-0.00012500
H	2.27326000	-1.20186200	-0.00031000
Sb	-0.39998900	-0.30197500	0.00003100
H	-0.59918200	-1.45412000	1.24285100
H	-0.59935300	-1.45405500	-1.24282200
Be	-1.77073600	2.06117900	-0.00008100
H	-0.78530100	2.97755800	0.00069500
H	-3.06203200	1.69052400	-0.00088100

Deprotonated (Sb) Vinylstibine:BeH₂

C	-2.66398600	0.33623400	0.33961200
H	-2.69094200	-0.25940400	1.24711100
H	-3.60152400	0.80967100	0.05260800
C	-1.54745700	0.49055800	-0.37490300
H	-1.60512800	1.11093800	-1.26902700
Sb	0.42245300	-0.33364400	-0.06227500
H	0.07243500	-0.87940700	1.53776300
Be	1.80130600	1.72455600	0.29421100
H	1.52195900	2.76085300	-0.57987500
H	2.82155400	1.61422500	1.22233900

Deprotonated (Be) Vinylstibine:BeH₂

C	-3.91488800	-0.01884400	-0.01931200
H	-4.22524300	1.02454300	-0.04561900
H	-4.73432600	-0.74271700	-0.03904700
C	-2.61856300	-0.35546300	0.03440000
H	-2.44857500	-1.43870900	0.05824300
Be	-1.30805000	0.79826200	0.07621200
H	-1.45764700	2.17816700	0.04545800
Sb	1.06994100	-0.02771100	-0.05072500
H	0.98703900	-1.44519400	0.93135100
H	1.74464900	0.88995800	1.24123700

Ethynylamine:BeH₂

C	-1.86450000	0.25963400	-0.00005000
H	-2.86535900	0.62656200	-0.00000700
C	-0.72397000	-0.12945600	0.00001800
N	0.59821700	-0.54275600	0.00003000
H	0.81383000	-1.11948500	-0.81695900
H	1.56378000	1.97407500	0.00019200
H	3.08845000	-0.10823000	-0.00025100
Be	1.98216400	0.69110400	-0.00006100
H	0.81394500	-1.11911800	0.81725300

Deprotonated (N) ethynylamine:BeH₂

C	1.86089900	0.20324000	-0.06152100
H	2.83166900	0.50760600	0.25451200
C	0.67114100	-0.10682900	0.01140000
N	-0.61396300	-0.43803100	0.00030800
H	-0.75195900	-1.44416300	0.02425000
H	-1.89094400	1.86450100	-0.00470700
H	-3.15915900	-0.31468900	0.01737700
Be	-1.98102700	0.46862400	0.00178500

Deprotonated (Be) ethynylamine:BeH₂

C	-2.11944400	-0.21555800	0.00005200
H	-3.13744300	-0.53759300	-0.00053700
C	-0.94872800	0.16753400	0.00005100
N	1.86546100	-0.37343600	0.00009900
H	1.71335300	-1.37560900	0.00003100
H	1.03733700	2.10022500	-0.00001700
H	2.85845600	-0.17479400	-0.00070300
Be	0.71977600	0.72249200	-0.00002000

Ethynylphosphine:BeH₂

C	-2.32012000	0.41550800	-0.00006300
H	-3.33017000	0.76162300	-0.00011900
C	-1.17966800	0.00170700	0.00000900
H	2.18997600	2.24050700	0.00040700
H	3.30046300	-0.11052100	-0.00053200
Be	2.40453100	0.91249700	-0.00011000
P	0.53662500	-0.42274600	0.00002800
H	0.58554300	-1.35154000	1.06498700
H	0.58541800	-1.35215500	-1.06439400

Deprotonated (P) ethynylphosphine:BeH₂

C	2.22245000	0.39962600	0.06220700
H	3.21325800	0.78548300	0.12454200
C	1.06309100	0.00589800	0.03274400
H	-1.76825500	2.26660100	-0.42748900
H	-3.23054300	0.54002000	0.66358200
Be	-2.04928900	1.01386500	0.09507800
P	-0.60439700	-0.58338000	-0.15771400
H	-0.66459900	-1.33000800	1.05505700

Deprotonated (Be) ethynylphosphine:BeH₂

C	-2.68383500	-0.36439700	0.00103500
H	-3.63727200	-0.83483900	-0.00611000
C	-1.60112000	0.19812600	0.00960600
H	0.06014900	2.35508300	0.03684100
Be	-0.07665400	0.98099700	0.03083400
P	1.70945800	-0.23598000	-0.11974800
H	2.55074900	0.41694900	0.82925200
H	1.40084200	-1.32385800	0.74905100

Ethynylarsine:BeH₂

C	2.63699600	0.41930300	0.00018400
H	3.67750500	0.65580000	0.00031300
C	1.45494200	0.15264700	0.00005500
H	-2.38070500	2.29997300	-0.00104600
H	-3.14806200	-0.18545100	0.00170700
Be	-2.41873200	0.95863000	0.00029900
As	-0.37056800	-0.22915400	-0.00008400
H	-0.39829000	-1.23686300	-1.11520300
H	-0.39841100	-1.23758600	1.11437500

Deprotonated (As) ethynylarsine:BeH₂

C	-2.52950500	0.46436500	0.06991200
H	-3.55563800	0.74722500	0.09798800
C	-1.35019500	0.14554200	0.02691100
H	1.43834200	2.59881700	-0.52183100
H	2.98881000	1.06738900	0.72323000
Be	1.79295700	1.41334200	0.09992800
As	0.44649800	-0.38665500	-0.07887600
H	0.50041300	-0.96661000	1.32285500

Deprotonated (Be) ethynylarsine:BeH₂

C	-3.31400300	-0.39351500	-0.00223700
H	-4.24542000	-0.91455200	-0.01748100
C	-2.23707000	0.20018800	0.01639500
H	-0.65166400	2.42667000	0.00808200
Be	-0.73824100	1.04104500	0.04725900
As	1.16066200	-0.11697700	-0.06413400
H	1.97978100	0.62415900	0.97976900
H	0.87485000	-1.28026900	0.87205900

Ethynylstibine:BeH₂

C	2.88015600	0.65211400	-0.00014800
H	3.88935600	0.98968000	-0.00022700
C	1.74408100	0.24925000	-0.00002800
Sb	-0.28801000	-0.23387100	0.00006200
H	-0.18282400	-1.39899800	1.24274400
H	-0.18332300	-1.39782200	-1.24372500
Be	-2.69981600	1.35869800	-0.00014600
H	-2.32227700	2.63993200	0.00106400
H	-3.45857500	0.25162800	-0.00137000

Deprotonated (Sb) ethynylstibine:BeH₂

C	-2.84812300	0.50813800	0.03900600
H	-3.87534500	0.77915200	0.03065500
C	-1.66912300	0.22407000	0.06622900
Sb	0.38370200	-0.31756400	-0.05355200
H	0.44645800	-0.76146900	1.60918700
Be	1.70236400	1.81665100	0.08098200
H	1.19995100	2.97383600	-0.47031500
H	2.95414300	1.54439900	0.60628900

Deprotonated (Be) ethynylstibine:BeH₂

C	3.71241400	-0.46214300	-0.00571000
H	4.59647100	-1.05251200	-0.02840600
C	2.69459800	0.20600200	0.02280200
H	-0.64722600	-1.33064300	1.10345500
H	-1.80157700	0.85638500	1.09800200
Sb	-0.91823700	-0.07905100	-0.04904300
Be	1.26157900	1.14358100	0.05670400
H	1.19404000	2.52090300	-0.00120100

Ethylamine:BH₃

C	1.55378600	-0.57655200	0.12010800
H	1.70764600	-0.56934300	1.20591400
H	2.53727900	-0.51086900	-0.35535600
H	1.09270800	-1.52646400	-0.15548800
C	0.69567400	0.60066300	-0.32559700
H	1.18592000	1.54962200	-0.07634600
H	0.53003500	0.57228600	-1.40569200
H	-0.56560700	0.55022600	1.31850800
H	-1.13643200	1.45537400	0.08992800
B	-1.69764600	-0.62935400	-0.15521400
H	-2.74678600	-0.33836400	0.38237600
H	-1.74456200	-0.55964100	-1.36641800
H	-1.23446900	-1.66950100	0.25464800
N	-0.66203700	0.57839700	0.30241900

Deprotonated Ethylamine:BH₃

C	1.89427500	-0.12605700	-0.05936000
H	2.07057300	-0.89445700	0.70716000
H	2.67709900	0.63975300	0.05230500
H	2.00700800	-0.60749600	-1.03859100
C	0.48611700	0.47435800	0.08350800
H	0.43774100	1.02124100	1.05711000
H	0.34767800	1.24701900	-0.68720500
B	-2.02165600	0.08853200	-0.04341900
H	-2.19779600	0.82914200	-1.02349200
H	-2.83898100	-0.84185500	-0.07011600
H	-2.21970300	0.76600200	1.00023000
H	-0.47242800	-1.20244200	0.64937000
N	-0.56932300	-0.49848200	-0.08208000

Ethylphosphine:BH₃

C	-1.88432600	0.67256900	-0.20003600
H	-1.41571300	1.64258600	-0.01364300
H	-2.89709700	0.69881300	0.21445100
H	-1.97203200	0.54170700	-1.28398500
C	-1.08223500	-0.46897100	0.44075000
H	-1.01958800	-0.33029900	1.52608400
H	-1.56248900	-1.43676200	0.26167300
P	0.66437900	-0.54826900	-0.16769200
H	1.11762400	-1.77580100	0.36286100
H	0.50247700	-0.92264800	-1.52065000
B	1.81786300	0.98457800	0.16934600
H	2.89043300	0.66813800	-0.29182000
H	1.28909100	1.90723300	-0.40733200
H	1.81166800	1.08660000	1.37673000

Deprotonated Ethylposphine: BH_3

C	2.24219100	0.01097800	0.03548800
H	2.36797400	-0.60264300	0.93718600
H	3.02924900	0.78149600	0.04764300
H	2.42189700	-0.64375800	-0.82636400
C	0.83494000	0.62011400	-0.02281600
H	0.67118900	1.28650600	0.83518000
H	0.74027100	1.24729600	-0.91965000
P	-0.57865400	-0.63697200	-0.12832300
H	-0.41213900	-1.13787000	1.20947300
B	-2.20773100	0.52519200	0.06460800
H	-2.32532500	1.12741100	-1.00073000
H	-3.16688700	-0.22138100	0.23761800
H	-2.07054300	1.30500800	1.00541700

Ethylarsine: BH_3

C	2.51670100	-0.00365600	0.00001500
H	2.60683800	-0.64255900	0.88475800
H	3.36897200	0.68507800	0.00007700
H	2.60692500	-0.64251000	-0.88475300
C	1.20080000	0.77687900	-0.00003500
H	1.12547000	1.42862400	0.87723600
H	1.12551400	1.42866500	-0.87727200
B	-2.25937700	0.64865300	0.00002300
H	-2.23277600	1.29963300	-1.01772900
H	-3.05156100	-0.26179600	0.00000900
H	-2.23262000	1.29966900	1.01773300
As	-0.42480500	-0.30179600	-0.00001000
H	-0.15318800	-1.25890200	1.12958800
H	-0.15314600	-1.25923100	-1.12932200

Deprotonated Ethylarsine: BH_3

C	-2.22591300	0.49393200	-0.32588800
H	-1.83949000	1.47447300	-0.62675200
H	-3.21965600	0.64773200	0.12231100
H	-2.36011400	-0.10029200	-1.23975900
C	-1.25860300	-0.19439700	0.64217400
H	-1.15726600	0.41127900	1.55148700
H	-1.65989400	-1.17453600	0.93337700
B	1.38017600	1.48114500	0.14928700
H	1.07664100	1.87828200	1.26956500
H	2.59405200	1.38457200	0.00984200
H	0.90091200	2.19143900	-0.72897100
As	0.56218900	-0.44715400	-0.15209400
H	1.11880000	-1.15980700	1.08383200

Ethylstibine: BH_3

C	2.76723200	0.05337600	0.00004300
H	2.82912500	-0.58757500	0.88121300
H	3.64970400	0.69903000	0.00004700
H	2.82921000	-0.58768400	-0.88104100
C	1.49233600	0.89020400	-0.00004200
H	1.43358400	1.53620100	0.87720200
H	1.43361800	1.53608600	-0.87736900
B	-2.39210100	0.86224300	0.00002700
H	-2.30126400	1.48857100	-1.02063200
H	-3.16702900	-0.05357300	0.00028500
H	-2.30094300	1.48878100	1.02054100
Sb	-0.35342400	-0.25162600	-0.00001200
H	0.01078600	-1.32968500	1.26805700
H	0.01093500	-1.32991200	-1.26784400

Deprotonated Ethylstibine: BH_3

C	-2.75118800	0.15216200	0.06701800
H	-2.87788100	-0.59539300	-0.72148700
H	-3.61604100	0.82968200	0.02112700
H	-2.80636800	-0.38041400	1.02074100
C	-1.42404900	0.89073000	-0.07629300
H	-1.37964700	1.42508100	-1.02911400
H	-1.29784200	1.63445000	0.71226400
B	1.99472800	1.30299100	0.08692800
H	1.63919600	2.10564600	0.92713500
H	3.04311000	0.75167600	0.36716900
H	2.01646000	1.77187200	-1.03801100
Sb	0.39539600	-0.38352900	-0.04473700
H	0.19161200	-0.75494900	1.64277700

Vinylamine: BH_3

C	-1.81467800	0.00203300	0.29595800
H	-1.90956600	0.89389900	0.90992900
H	-2.67002300	-0.66201000	0.24811900
C	-0.69565600	-0.29745400	-0.35633900
H	-0.57175400	-1.19808900	-0.94797300
N	0.51246800	0.49561100	-0.28866200
H	0.78916200	0.79408700	-1.22502600
H	0.35175500	1.34101900	0.25864700
B	1.84424000	-0.30606500	0.35170500
H	1.99154200	-1.27265000	-0.36379300
H	2.73667000	0.50941200	0.25535400
H	1.53574200	-0.57209000	1.48914400

Deprotonated Vinylamine: BH_3

C	-1.94317200	-0.06355200	0.00028100
H	-2.21990800	-1.11685900	0.00032100
H	-2.74538100	0.66683300	-0.00036200
C	-0.63118100	0.34850200	-0.00004100
H	-0.43422300	1.42286500	-0.00058600
N	0.49793300	-0.38137600	-0.00038500
H	0.33935800	-1.38324400	-0.00002700
B	1.98042900	0.12110000	0.00014000
H	2.57488500	-0.29239700	1.00746400
H	2.57615500	-0.29516100	-1.00506900
H	1.96755400	1.35239500	-0.00118400

Vinylphosphine: BH_3

C	-1.82075100	0.74516300	0.00033600
H	-1.24904300	1.66913500	0.00158600
H	-2.90435400	0.83101000	-0.00012300
C	-1.22298100	-0.45038500	-0.00066800
H	-1.80852600	-1.36803300	-0.00204900
P	0.59154600	-0.59882100	0.00030500
H	0.82829600	-1.48851200	-1.07141900
B	1.64932600	1.03937700	-0.00052000
H	1.32935800	1.60906500	-1.01834300
H	1.32842000	1.61073800	1.01608300
H	2.79105300	0.63994600	0.00043600
H	0.82736700	-1.48658900	1.07385000

Deprotonated (P) Vinylphosphine: BH_3

C	2.16890500	0.20470400	0.28225300
H	2.31885200	-0.51270000	1.08794700
H	3.02310500	0.83135000	0.02589300
C	0.98612300	0.31751900	-0.35757400
H	0.91886400	1.07372300	-1.14558000
P	-0.55418800	-0.64549000	-0.18842000
H	-0.22300500	-1.26435300	1.06157200
B	-1.97910600	0.71473700	0.26075900
H	-1.65967000	1.38627300	1.23172600
H	-2.10265900	1.39861400	-0.75045700
H	-2.99731100	0.06241700	0.46333600

Deprotonated (B) Vinylphosphine: BH_3

C	-2.39614200	-0.26765400	0.26494400
H	-2.54023000	0.13977400	1.26693400
H	-3.21035700	-0.88686400	-0.12039500
C	-1.27280600	-0.00613900	-0.43462300
H	-1.23453100	-0.47140100	-1.43085500
H	-0.16433700	1.38588500	1.12018900
P	1.65497800	-0.28771100	-0.04704700
H	1.56590500	-1.00813300	1.19008200
H	2.62619400	0.62947000	0.47106100
B	-0.01672000	0.88549000	0.01260100
H	0.22997400	1.74224100	-0.83624200

Vinylarsine: BH_3

C	-2.14354800	0.76752000	-0.00000700
H	-1.64438300	1.73298100	0.00001400
H	-3.23092100	0.77503200	0.00016200
C	-1.45968800	-0.37858000	-0.00004300
H	-1.97711800	-1.33530900	0.00000500
As	0.45650900	-0.39317300	0.00000100
H	0.76310800	-1.34164400	-1.12706500
H	0.76334900	-1.34128300	1.12734100
B	1.43506500	1.42719600	-0.00000100
H	2.59962500	1.11150300	-0.00118200
H	1.05201600	1.95230900	-1.01796800
H	1.05362400	1.95149300	1.01895500

Deprotonated (As) Vinylarsine: BH_3

C	2.42064200	0.33967200	0.27589600
H	2.52378100	-0.18415000	1.22536500
H	3.31001100	0.85459200	-0.08942000
C	1.25822700	0.36051300	-0.40072800
H	1.25455100	0.92396900	-1.33907500
As	-0.44204100	-0.46866700	-0.06270100
H	-0.11913200	-0.85136300	1.38215500
B	-1.72153400	1.21637600	0.19689900
H	-1.23958000	1.98722900	1.00934800
H	-2.78852700	0.74326600	0.56519500
H	-1.81928900	1.70946800	-0.91992500

Deprotonated (B) Vinylarsine: BH_3

C	-2.79775400	-0.45882800	0.22302600
H	-2.85817900	-0.41543500	1.31142600
H	-3.56836500	-1.05292400	-0.27481400
C	-1.82131400	0.19260300	-0.44205100

H	-1.84845000	0.07712400	-1.53529700
H	-0.79503700	1.27770200	1.38728800
H	0.95477100	-1.14686300	1.08566100
H	2.10504000	0.67145400	0.77845000
B	-0.62482400	1.03869200	0.20168800
H	-0.36680000	2.05128200	-0.44180700
As	1.12774400	-0.15328600	-0.06076400

Vinylstibine:BH₃

C	-2.42796400	0.85297300	0.00000400
H	-1.93567000	1.81914800	-0.00000200
H	-3.51347900	0.86904500	0.00002300
C	-1.75499700	-0.29051500	-0.00001600
H	-2.27567100	-1.24203300	-0.00001500
Sb	0.37948100	-0.32037100	0.00000200
H	0.63138800	-1.43520600	-1.26213600
H	0.63132800	-1.43523800	1.26212500
B	1.48611500	1.72454200	-0.00000100
H	2.63088400	1.36660900	-0.00027600
H	1.07223300	2.19966800	-1.02164400
H	1.07265600	2.19948800	1.02189400

Deprotonated (Sb) Vinylstibine:BH₃

C	-2.69128000	0.38157200	0.29440400
H	-2.72017800	-0.12374200	1.25530000
H	-3.62619100	0.83688200	-0.03065000
C	-1.57608600	0.45207700	-0.43342500
H	-1.63271300	0.98602600	-1.38284700
Sb	0.38719200	-0.37858500	-0.04157100
H	-0.00300300	-0.74315900	1.60899400
B	1.65631600	1.57093300	0.18420600
H	2.74556900	1.16696200	0.54670600
H	1.12095100	2.30778500	0.98223000
H	1.69138100	2.02052900	-0.94649000

Deprotonated (B) Vinylstibine:BH₃

C	-3.27680500	-0.44325600	0.24373200
H	-3.43094100	-0.22148900	1.29710800
H	-4.00190100	-1.11459500	-0.21336500
C	-2.24639300	0.08521300	-0.43174000
H	-2.19074800	-0.20805000	-1.48633100
H	-1.27569300	1.42614800	1.26075400
H	0.87351500	-1.01171300	1.43536400
H	1.94452700	1.08845000	0.71551100
B	-1.12652400	1.07061700	0.11193700

H	-0.89941000	1.99560100	-0.64936000
Sb	0.93632300	-0.10116000	-0.03512400

Ethynylamine:BH₃

C	1.93226300	-0.29137300	-0.00000300
H	2.91989900	-0.69282900	-0.00006800
C	0.81042000	0.14634200	0.00003800
N	-0.49662100	0.61712400	-0.00001200
H	-0.66449900	1.19861100	-0.82318900
H	-0.66453600	1.19866800	0.82311800
B	-1.74392700	-0.57810400	0.00000100
H	-1.55896200	-1.19231400	-1.01975400
H	-1.55900900	-1.19224300	1.01980700
H	-2.73300300	0.12093800	-0.00004600

Deprotonated (N) Ethynylamine:BH₃

C	-1.96599000	-0.23710200	-0.11252700
H	-2.78144300	-0.57945000	0.49702400
C	-0.77638500	0.12233300	0.01787000
N	0.47411000	0.50666200	-0.01394800
H	0.60831700	1.50094800	0.12849800
B	1.78858300	-0.39500700	0.00416700
H	2.03169200	-0.77273200	1.15538100
H	1.62793000	-1.35532300	-0.73861500
H	2.70607200	0.32357200	-0.39754300

Deprotonated (B) Ethynylamine:BH₃

C	-2.00859100	-0.25845100	0.00136100
H	-3.00822900	-0.62981100	0.00357800
C	-0.85919000	0.17618300	-0.00513700
N	1.72414100	-0.44502900	0.00053300
H	1.60309900	-1.04780700	-0.81304400
B	0.66219100	0.70610400	0.00157700
H	0.82157700	1.41045800	-0.99930900
H	0.81254700	1.39956500	1.01144300
H	1.59775000	-1.05411500	0.80837900

Ethynylphosphine:BH₃

C	2.32795500	0.41368600	0.00000000
H	3.33082100	0.78036200	0.00000300
C	1.19377900	-0.01480200	0.00000000
B	-1.90865200	0.84745900	0.00000000
H	-1.73589200	1.46548000	1.02117500
H	-1.73589200	1.46547900	-1.02117500
H	-2.89362400	0.14138800	0.00000000

P	-0.50023400	-0.50977900	0.00000000
H	-0.52452300	-1.41830900	-1.07960300
H	-0.52452200	-1.41830800	1.07960400

Deprotonated (P) Ethynylphosphine: BH_3

C	-2.27802100	0.41221000	0.00536700
H	-3.26499200	0.81275500	0.01780900
C	-1.12885500	-0.00874600	0.02552400
B	1.80403600	0.90099100	0.03809000
H	1.73955000	1.49953700	-1.02571600
H	1.53183400	1.60735700	0.99489800
H	2.89216400	0.34748100	0.16313000
P	0.53117300	-0.66503000	-0.11538000
H	0.55492500	-1.21740800	1.20478500

Deprotonated (B) Ethynylphosphine: BH_3

C	-2.46522000	-0.42713600	-0.01282400
H	-3.38697600	-0.96147700	-0.03430000
C	-1.40411700	0.18581600	0.01159700
B	-0.03785300	0.96717400	0.04146900
H	0.07261900	1.68600300	-0.94315100
H	0.06874200	1.62552900	1.06406700
P	1.50339900	-0.35549400	-0.11225600
H	2.58723700	0.53062700	0.19817900
H	1.51267600	-0.93622200	1.19905800

Ethynylarsine: BH_3

C	2.59336600	0.50145000	-0.00000300
H	3.61314800	0.81575800	0.00001800
C	1.43288200	0.15458600	-0.00000200
B	-1.85160900	1.11318200	0.00000000
H	-1.64329800	1.71369700	1.02302900
H	-1.64330000	1.71369400	-1.02303200
H	-2.83136100	0.40621300	0.00000200
As	-0.35420600	-0.34826000	0.00000000
H	-0.35291800	-1.32944500	1.13643300
H	-0.35291900	-1.32944800	-1.13642900

Deprotonated (As) Ethynylarsine: BH_3

C	2.55244600	0.48628000	0.01215200
H	3.56843100	0.80557300	0.00905300
C	1.38247900	0.13379800	0.00531500
B	-1.56897800	1.33528300	0.03385800

H	-2.70370900	0.90530600	0.20246100
H	-1.18928400	2.04559300	0.94601400
H	-1.44130300	1.85162800	-1.06515500
As	-0.41151300	-0.45852900	-0.05398900
H	-0.41887900	-0.87351300	1.41518500

Deprotonated (B) Ethynylarsine: BH_3

C	-2.55241000	0.48603100	0.01219200
H	-3.56841100	0.80526100	0.00889900
C	-1.38243000	0.13361400	0.00531300
B	1.56830100	1.33535000	0.03383600
H	1.44074400	1.85197700	-1.06487900
H	1.18825600	2.04533500	0.94597700
As	0.41165300	-0.45847700	-0.05400000
H	2.70331800	0.90616100	0.20267200
H	0.41907800	-0.87360900	1.41511500

Ethynylstibine: BH_3

C	-2.85379400	0.62775800	0.00007600
H	-3.86146400	0.97029700	0.00057700
C	-1.71768400	0.22727400	-0.00036900
B	1.92098000	1.39533100	-0.00000600
H	1.65096900	1.95364800	-1.02461600
H	1.65065000	1.95401100	1.02432000
H	2.89536400	0.69409800	0.00026100
Sb	0.29469800	-0.29092500	0.00001800
H	0.22961900	-1.42105000	-1.26913100
H	0.22923300	-1.42068100	1.26947300

Deprotonated (Sb) Ethynylstibine: BH_3

C	-2.87037700	0.52654200	-0.00563500
H	-3.89245800	0.81543600	-0.03516400
C	-1.69708800	0.22306500	0.04786600
B	1.52016500	1.65405500	0.03618500
H	1.38938400	2.12554000	-1.07491800
H	1.08384200	2.34837900	0.92433100
H	2.65554700	1.25913900	0.23718900
Sb	0.35691100	-0.36351700	-0.04167200
H	0.36520100	-0.77704400	1.63950000

Deprotonated (B) Ethynylstibine: BH_3

C	-3.27093100	-0.59154500	-0.00829900
H	-4.08466400	-1.27323100	-0.02335500
C	-2.33644900	0.18474300	0.01145600
H	-1.05358200	1.84457700	-0.97095700
H	1.96725500	1.14210700	0.30422500
H	0.89511900	-0.65024800	1.60459000
B	-1.13119600	1.17353900	0.03801300
H	-1.08482600	1.84675900	1.04128600
Sb	0.83648900	-0.12425200	-0.04244700

Table S2. LMO-EDA partition terms (kJ mol^{-1}) for the complexes formed by association of $\text{CH}_2=\text{CHXH}_2$ ($\text{X} = \text{N}, \text{P}, \text{As}$) and its deprotonated anions with BeH_2 and BH_3 .

Complex	E_{int}	ΔE_{elstat}	$\Delta E_{\text{ex+rep.}}$	$\Delta E_{\text{pol.}}$	ΔE_{disp}
$\text{CH}_2=\text{CHXH}_2:\text{BeH}_2$					
$\text{X} = \text{N}$	-113	-211	235	-127	-10
$\text{X} = \text{P}$	-71	-133	186	-118	-6
$\text{X} = \text{As}$	-50	-102	151	-93	-6
$[\text{CH}_2=\text{CHXH}:\text{BeH}_2]^-$					
$\text{X} = \text{N}$	-354	-449	350	-247	-8
$\text{X} = \text{P}$	-230	-271	265	-218	-6
$\text{X} = \text{As}$	-210	-253	254	-205	-6
$\text{CH}_2=\text{CHXH}_2:\text{BH}_3$					
$\text{X} = \text{N}$	-158	-303	448	-290	-13
$\text{X} = \text{P}$	-160	-271	503	-382	-10
$\text{X} = \text{As}$	-116	-213	404	-299	-9
$[\text{CH}_2=\text{CHXH}:\text{BH}_3]^-$					
$\text{X} = \text{N}$	-365	-490	623	-498	-10
$\text{X} = \text{P}$	-271	-327	520	-454	-10
$\text{X} = \text{As}$	-244	-298	475	-410	-11

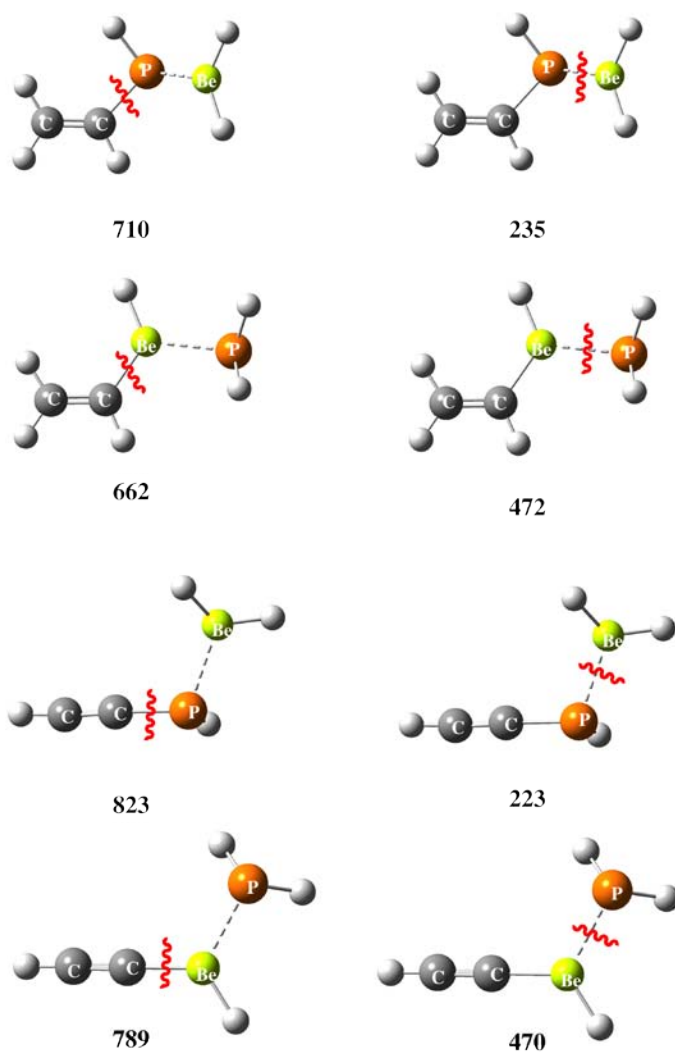


Figure S1. LMO-EDA Interaction energies (kJ mol⁻¹) between the fragments resulting from the bond fissions indicated by the wiggled red line.

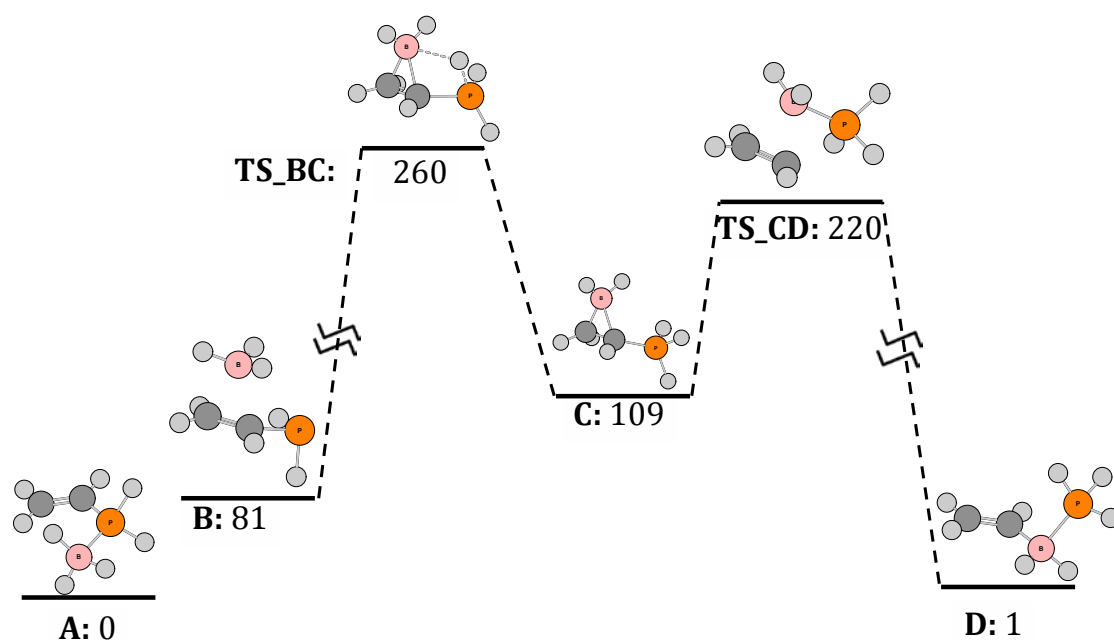


Figure S2-a. Mechanism to form the insertion-complex **D** starting from the vinylphosphine: BH_3 π -complex **B**. Deprotonation of the *insertion-complex* leads to formation of the most stable anion, $[\text{R-YH}_2\text{-XH}_2]^-$, insertion anion.

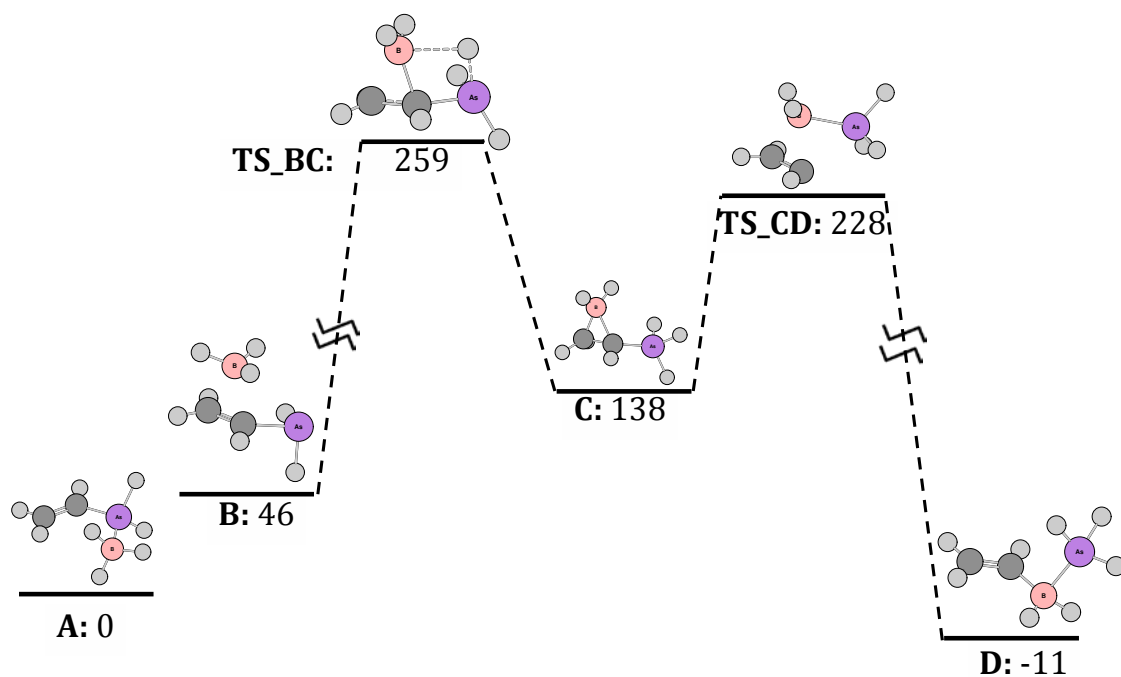


Figure S2-b. Mechanism to form the insertion-complex **D** starting from the vinylarsinine: BH_3 π -complex **B**. Deprotonation of the *insertion-complex* leads to formation of the most stable anion, $[\text{R-YH}_2\text{-XH}_2]^-$, insertion anion.

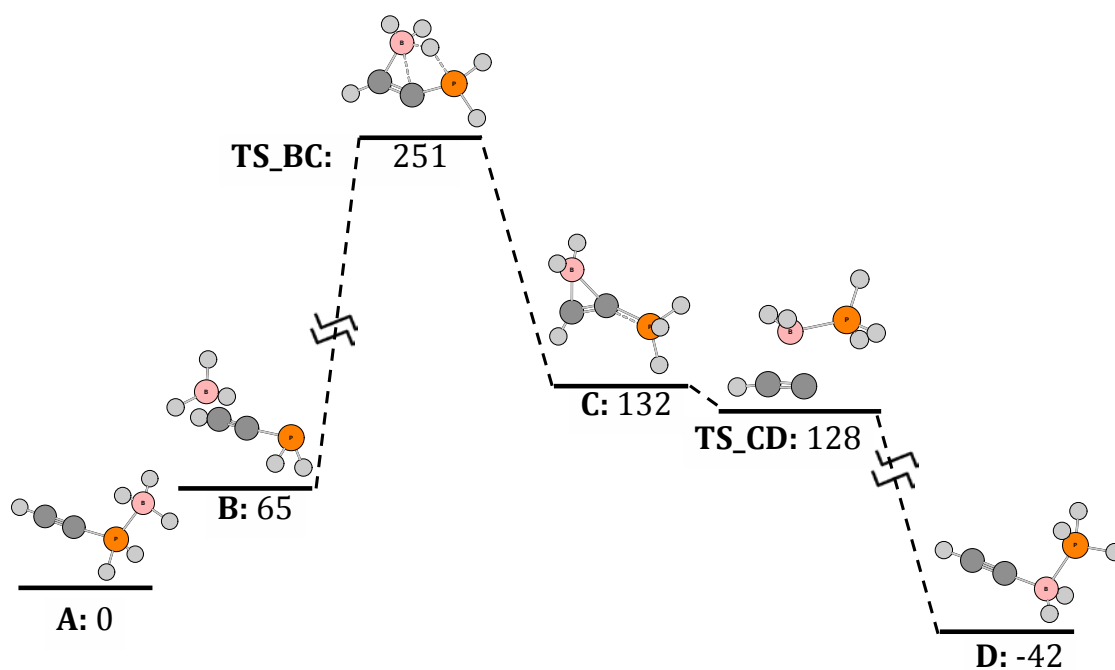


Figure S2-c. Mechanism to form the insertion-complex **D** starting from the ethynylphosphine:BH₃ π -complex **B**. Deprotonation of the *insertion-complex* leads to formation of the most stable anion, [R-YH₂-XH₂]⁻, insertion anion.