Methane C—H Bond Activation by "Naked" Alkali Metal Imidyl and Alkaline Earth Metal Imide Complexes. The Role of Ligand Spin and Nucleophilicity.

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Cartesian Coordinates (Å)
Level of theory used for geometry optimization: B3LYP/cc-pVTZ

Imidyl [NH^-] reaction optimized geometries

$^2NH^-$

7	0.000000000	0.000000000	0.131693000
1	0.000000000	0.000000000	-0.921850000

Methane

6	0.000000000	0.000000000	0.000000000
1	0.628170000	0.628170000	0.628170000
1	-0.628170000	-0.628170000	0.628170000
1	-0.628170000	0.628170000	-0.628170000
1	0.628170000	-0.628170000	-0.628170000

Doublet $NH^-...(CH_4)$ – Methane Adduct

6	1.456413000	-0.002248000	-0.004450000
1	1.751342000	1.043779000	-0.133663000
1	1.853441000	-0.361610000	0.950316000
1	1.901438000	-0.592943000	-0.811549000
7	-1.830458000	-0.124801000	-0.047463000
1	0.339079000	-0.093644000	-0.022575000
1	-1.778005000	0.913305000	0.069145000

Doublet TS – NH(H)...(CH_3) anion

6	1.336366000	0.010963000	-0.013532000
1	1.665061000	1.039211000	-0.221376000
1	1.720991000	-0.266353000	0.979926000
1	1.811807000	-0.648129000	-0.754222000
7	-1.375139000	-0.039904000	-0.265447000
1	-0.070254000	-0.137258000	-0.024414000
1	-1.573419000	0.809128000	0.299244000

Product – NH_2^- separated from $^2CH_3$

6	-1.526100000	0.000000000	0.062843000
1	-1.472421000	0.910422000	-0.531342000
1	-1.472422000	-0.910423000	-0.531341000
1	-0.886301000	0.000000000	0.938919000
7	1.490942000	0.000000000	0.110096000
1	1.275575000	0.787730000	-0.511982000
1	1.275574000	-0.787729000	-0.511983000

Singlet – NH_2^- - amide

7	0.000000000	0.000000000	0.149969000
1	0.000000000	0.789440000	-0.524892000

1	0.000000000	-0.789440000	-0.524892000

Doublet CH_3

6	0.000000000	0.000000000	0.000023000
1	0.000000000	1.078026000	-0.000046000
1	-0.933598000	-0.539013000	-0.000046000
1	0.933598000	-0.539013000	-0.000046000

Nitrene [NH^0] reaction optimized geometries

^3NH

7	0.000000000	0.000000000	0.130132000
1	0.000000000	0.000000000	-0.910923000

Triplet TS – NH(H)(CH_3)

6	-2.331070000	0.410654000	-0.008564000
1	-1.439011000	-0.197076000	0.088642000
1	-2.584806000	0.989845000	0.871773000
1	-3.169176000	-0.086772000	-0.482625000
7	-1.630790000	2.201913000	-1.785381000
1	-1.966528000	1.442485000	-0.918995000
1	-1.401549000	1.531253000	-2.538316000

Product - $^2NH_2$ separated from $^2CH_3$

6	-1.711035000	-0.012428000	0.000026000
1	-1.726192000	-0.543579000	0.938345000
1	-1.797059000	1.062518000	-0.009956000
1	-1.723971000	-0.560753000	-0.928395000
7	1.827455000	0.111187000	0.000293000
1	0.806614000	0.251080000	-0.001886000
1	1.914629000	-0.913011000	-0.000317000

$^2NH_2$ - aminyl

7	0.000000000	0.000000000	0.142608000
1	0.000000000	0.802925000	-0.499126000
1	0.000000000	-0.802925000	-0.499126000

LiNH + CH_4 → $LiNH_2$ + CH_3 reaction optimized geometries

^2LiNH

3	-0.000029000	1.325243000	0.000000000
7	-0.000029000	-0.370030000	0.000000000
1	0.000288000	-1.385518000	0.000000000

$^2LiNH(CH_4)$ Methane Adduct

3	0.739747000	1.254089000	-4.380106000
7	0.476917000	1.016552000	-6.042898000
1	0.268464000	0.946602000	-7.034281000
6	2.155389000	-2.015432000	-8.027761000
1	3.105337000	-2.340866000	-7.605770000
1	2.318891000	-1.656272000	-9.042835000
1	1.465717000	-2.857980000	-8.051962000
1	1.737726000	-1.216148000	-7.416735000

Doublet TS – LiNH(H)(CH_3) - HAA

3	0.695184000	-0.279004000	-4.739287000
7	0.898723000	0.052892000	-6.405342000
1	0.758476000	0.682803000	-7.189608000
6	2.055223000	-1.819094000	-7.763801000
1	3.072663000	-1.480035000	-7.928387000
1	1.465212000	-1.869310000	-8.672799000
1	1.998403000	-2.732088000	-7.176640000
1	1.469165000	-0.875289000	-6.994855000

Doublet TS – $LiNH(H)(CH_3)$ – [2+2]

3	-0.573702000	0.286544000	-4.711249000
7	0.791494000	0.271021000	-5.772019000
1	1.526314000	-0.178743000	-6.311306000
6	1.396699000	-0.042592000	-3.259913000
1	0.462519000	-0.007241000	-2.686541000
1	2.072162000	0.738196000	-2.921624000
1	1.837093000	-1.032023000	-3.205654000
1	1.245486000	0.301802000	-4.625873000

Product – $^1LiNH_2$ separated $^2CH_3$

3	-0.799877000	0.025437000	-6.042454000
7	0.886286000	0.396983000	-6.114548000
1	1.365530000	0.977832000	-6.794679000
6	2.308728000	-2.435447000	-8.096066000
1	2.638517000	-3.339614000	-7.607224000
1	1.936115000	-1.600904000	-7.516008000
1	2.373560000	-2.370429000	-9.171625000
1	1.602857000	0.165888000	-5.434278000

$LiNH_2$

3	-0.000091000	1.394827000	0.000000000
7	-0.000091000	-0.326618000	0.000000000
1	0.000455000	-0.949078000	0.801200000
1	0.000455000	-0.949078000	-0.801200000

$NaNH + CH_4 \rightarrow NaNH_2 + CH_3$ reaction optimized geometries

^2NaNH Linear

11	0.000000000	0.000000000	0.919755000
7	0.000000000	0.000000000	-1.137189000
1	0.000000000	0.000000000	-2.156986000

^2NaNH Bent

11	0.048118000	-0.939828000	0.000000000
7	0.048118000	1.232968000	0.000000000
1	-0.866117000	1.707331000	0.000000000

$^2NaNH(CH_4)$ Adduct

11	0.458335000	1.677225000	-4.139019000
7	0.717805000	0.699721000	-6.064963000
1	0.233932000	1.093842000	-6.883909000
6	2.170123000	-2.065302000	-8.100939000
1	3.132603000	-2.385533000	-7.702788000
1	2.306819000	-1.712459000	-9.122783000
1	1.485582000	-2.913096000	-8.104960000
1	1.762988000	-1.263852000	-7.482988000

Doublet TS – $NaNH(H)(CH_3)$ – HAA

11	-1.321734000	0.057102000	-5.471016000
7	0.795561000	0.508109000	-5.588786000
1	1.378916000	-0.182163000	-6.075259000
6	1.599785000	-0.050519000	-3.187258000
1	0.791408000	0.179161000	-2.496680000
1	2.483439000	0.553375000	-3.000644000
1	1.820370000	-1.112459000	-3.228749000
1	1.210319000	0.384357000	-4.445787000

Product - $NaNH_2$ separated from $^2CH_3$

11	-1.135426000	0.406828000	-5.819024000
7	0.949413000	0.215446000	-6.228248000
1	1.399424000	0.929609000	-6.797234000
6	2.372426000	-2.455017000	-8.119608000
1	2.812505000	-3.309767000	-7.627043000
1	1.940226000	-1.643599000	-7.543279000
1	2.386524000	-2.417630000	-9.199022000
1	1.586625000	0.093876000	-5.443424000

$^1NaNH_2$

11	-0.038878000	-1.003969000	0.000000000
7	-0.038878000	1.117643000	0.000000000
1	0.349905000	1.610078000	0.801429000
1	0.349905000	1.610078000	-0.801429000

BeNH + CH_4 → $BeNH_2$ + CH_3 reaction optimized geometries

^1BeNH

4	0.000146000	0.980526000	0.000000000
7	0.000146000	-0.365536000	0.000000000
1	-0.001607000	-1.363353000	0.000000000

Singlet TS – $BeNH(H)(CH_3)$ HAA

7	0.919899000	-0.023941000	-6.383523000
1	0.621105000	0.740115000	-6.978888000
6	2.121554000	-1.895545000	-7.851608000
1	3.128370000	-1.512355000	-7.965883000
1	1.519406000	-1.879327000	-8.752349000
1	2.044349000	-2.810597000	-7.276137000
1	1.443192000	-0.841326000	-7.003047000
4	0.731004000	-0.106761000	-4.924936000

Product – $^1H_2NBeCH_3$

7	-1.579993000	0.000000000	-0.000728000
1	-2.165377000	-0.820453000	-0.002447000
6	1.607613000	-0.000001000	0.001144000
1	2.035250000	-0.000193000	1.007153000
1	2.011785000	0.875714000	-0.516098000
1	2.011796000	-0.875506000	-0.516442000
1	-2.165371000	0.820458000	-0.002447000
4	-0.078453000	-0.000004000	0.007128000

$^2BeNH_2$

4	-0.000008000	1.123870000	0.000000000
7	-0.000008000	-0.370172000	0.000000000
1	0.000042000	-0.952137000	0.824221000
1	0.000042000	-0.952137000	-0.824221000

MgNH + CH_4 → $MgNH_2$ + CH_3 reaction optimized geometries

^1MgNH

12	-0.128088000	-0.604934000	0.250153000
7	0.248142000	1.117060000	-0.361193000
1	-0.174766000	1.803292000	0.278132000

Singlet $MgNH(CH_4)$ Methane Adduct

7	-0.589712000	0.707934000	0.154260000
1	-0.470031000	1.271001000	-0.698410000
6	2.989723000	-0.188423000	-0.009856000
1	3.353280000	-0.426421000	0.988936000
1	3.493491000	0.708171000	-0.368721000
1	3.213427000	-1.017440000	-0.680448000
1	1.913346000	-0.018119000	0.022632000
12	-2.109489000	-0.361849000	-0.023723000

Singlet TS – $MgNH(H)(CH_3)$ - HAA

7	0.956265000	-0.179020000	-6.358761000
1	0.084259000	-0.148966000	-6.890619000
6	2.162954000	-1.818423000	-7.912913000
1	3.199536000	-1.686193000	-7.634083000
1	1.848938000	-1.303278000	-8.807946000
1	1.744661000	-2.804322000	-7.755065000
1	1.488921000	-1.066252000	-6.712936000
12	0.855622000	0.693917000	-4.633508000

Singlet TS – $MgNH(H)(CH_3)$ - [2+2]

7	0.871556000	0.080216000	-5.851911000
1	1.185996000	-0.232490000	-6.763203000
6	1.297996000	-0.045104000	-3.161407000
1	0.518389000	-0.527359000	-2.570578000
1	1.599781000	0.883870000	-2.676084000
1	2.165178000	-0.706496000	-3.129662000
1	1.263476000	-0.118850000	-4.468512000
12	-0.216200000	1.009765000	-4.707934000

Product – $^1H_2NMgCH_3$

7	-1.954086000	0.000092000	-0.001162000
1	-2.556865000	-0.810754000	-0.000550000
6	2.030597000	0.000035000	-0.000385000
1	2.434908000	-0.040213000	1.013735000
1	2.430988000	0.899159000	-0.475210000
1	2.431316000	-0.858166000	-0.545408000
1	-2.556615000	0.811124000	-0.000541000
12	-0.057393000	-0.000167000	0.001534000

ccCA-calculated enthalpies (H, kcal/mol) for reaction of imidyl ($NH^{-\bullet}$) or imidogen ($NH^{\bullet\bullet}$) with methane using different basis set extrapolation schemes

Species	charge	multiplicity	ccCA-P	ccCA-S4	ccCA-S3	ccCA-PS3
NH^-	-1	2	79.4	80.4	80.4	79.9
CH_4	0	1	-18.0	-17.4	-17.6	-17.8
HAA TS	-1	2	64.9	66.6	66.2	65.6
NH_2^-	-1	1	24.4	25.5	25.2	24.8
CH_3	0	2	35.0	35.7	35.5	35.3

Species	charge	multiplicity	ccCA-P	ccCA-S4	ccCA-S3	ccCA-PS3
NH	0	3	85.9	86.9	87.1	86.5
HAA TS	0	3	87.3	89.0	88.9	88.1
NH_2	0	2	44.2	45.3	45.2	44.7

The ccCA-P, ccCA-S4, ccCA-S3 and ccCA-PS3 enthalpies employ different complete basis set extrapolation schemes, and are listed below:

The Peterson exponential/Gaussian scheme:[i]

$$E(x) = E_{CBS} + B \exp[-(x-1)] + C \exp[-(x-1)^2] \quad \text{(a)}$$

The Schwartz extrapolations of power four (S4) and three (S3):[ii]

$$E(l_{max}) = E_{CBS} + \frac{B}{(l_{max}+(\frac{1}{2}))^4} \quad \text{(b)}$$

$$E(l_{max}) = E_{CBS} + \frac{B}{(l_{max})^3} \quad \text{(c)}$$

The ccCA energies that utilize an averaging of Equation (a) and Equation (c) to compute the MP2 CBS energy is abbreviated as **ccCA-PS3**.[iii]

i. "Benchmark calculations with correlated molecular wave functions. IV. The classical barrier height of the $H+H_2 \rightarrow H_2+H$ reaction;" K.A. Peterson, D.E. Woon, and T.H. Dunning Jr. *J. Chem. Phys.* **1994**, *100*, 7410-7415.

ii. "Importance of Angular Correlations between Atomic Electrons;" C. Schwartz, *Phys. Rev. A* **1962**, *126*, 1015-1019.

iii. DeYonker, N. J.; Wilson, B. R.; Pierpont, A. W.; Cundari, T. R.; Wilson, A. K. Towards the Intrinsic Error of the correlation consistent Composite Approach (ccCA). *Mol. Phys.* **2009***, 107*, 1107-1121.

ccCA-calculated enthalpies (H, kcal/mol) for reaction of lithium imidyl with methane						
Compound	charge	multiplicity	ccCA-P	ccCA-S4	ccCA-S3	ccCA-PS3
LiNH $C_{\infty v}$	0	2	-4624.7	-4623.6	-4623.7	-4624.2
LiNH(CH_4) Adduct	0	2	-4642.1	-4640.4	-4640.8	-4641.5
LiNH(H)(CH_3) – TS –HAA	0	2	-4631.4	-4629.7	-4630.1	-4630.7
LiNH(H)(CH_3) – TS – [2+2]	0	2	-4630.0	-4628.3	-4628.7	-4629.3
$NH_2(CH_3)$	0	2	-4645.6	-4643.8	-4644.3	-4644.9
$LiNH_2$	0	1	-4680.2	-4679.1	-4679.4	-4679.8
$LiCH_3$	0	1	-4664.0	-4663.3	-4663.7	-4663.8
CH_3	0	2	35.0	35.7	35.5	35.3
NH_2	0	2	44.2	45.3	45.2	44.7
CH_4	0	1	-18.0	-17.4	-17.6	-17.8

ccCA-calculated enthalpies (H, kcal/mol) for reaction of sodium imidyl with methane						
Compound	Charges	multiplicity	ccCA-P	ccCA-S4	ccCA-S3	ccCA-PS3
NaNH $C_{\infty v}$	0	2	-101798.2	-101797.1	-101797.2	-101797.7
NaNH C_{2v}	0	2	-101797.4	-101796.4	-101796.4	-101796.9
NaNH(CH_4) Adduct	0	2	-101818.1	-101816.4	-101816.8	-101817.5
NaNH(H)(CH_3) – TS –HAA	0	2	-101805.6	-101803.9	-101804.3	-101804.9
$NH_2(CH_3)$	0	2	-101818.5	-101816.7	-101817.1	-101817.8
$NaNH_2$	0	1	-101852.5	-101851.4	-101851.7	-101852.1
$NaCH_3$	0	1	-101844.0	-101843.3	-101843.6	-101843.8
CH_3	0	2	35.0	35.7	35.5	35.3
NH_2	0	2	44.2	45.3	45.2	44.7
CH_4	0	1	-18.0	-17.4	-17.6	-17.8

ccCA-calculated enthalpies (H, kcal/mol) for reaction of beryllium imide with methane						
Compound	Charges	multiplicity	ccCA-P	ccCA-S4	ccCA-S3	ccCA-PS3
BeNH $C_{\infty v}$	0	1	-9105.1	-9103.9	-9104.3	-9104.7
BeNH(H)CH_3 TS - HAA	0	1	-9115.6	-9113.9	-9114.4	-9115.0
H_3C-Be-NH_2	0	1	-9215.8	-9214.1	-9214.8	-9215.3
$BeNH_2$	0	2	-9158.6	-9157.5	-9157.9	-9158.3
$BeCH_3$	0	2	-9138.4	-9137.7	-9138.1	-9138.2
CH_3	-1	1	33.0	33.6	33.4	33.2
NH_2	0	2	44.2	45.3	45.2	44.7
CH_4	1	0	-18.0	-17.4	-17.6	-17.8

ccCA-calculated enthalpies (H, kcal/mol) for reaction of magnesium imide with methane						
Compound	Charges	multiplicity	ccCA-P	ccCA-S4	ccCA-S3	ccCA-PS3
MgNH C_s	0	1	-125557.1	-125556.0	-125556.3	-125556.7
MgNH(CH_4)	0	1	-125574.7	-125573.0	-125573.5	-125574.1
MgNH(H)CH_3 TS – HAA	0	1	-125569.3	-125567.6	-125568.1	-125568.7
MgNH(H)CH_3 TS – [2+2]	0	1	-125566.2	-125564.4	-125565.0	-125565.6
N_2H-Mg-CH_3	0	1	-125642.7	-125640.9	-125641.5	-125642.1
$MgNH_2$	0	2	-125611.7	-125610.7	-125611.0	-125611.4
$MgCH_3$	0	2	-125599.2	-125598.6	-125598.9	-125599.1
CH_3	-1	1	33.0	33.6	33.4	33.2
NH_2	0	2	44.2	45.3	45.2	44.7
CH_4	0	1	-18.0	-17.4	-17.6	-17.8