# Electronic Supplementary Material (ESI) for New Journal of Chemistry

## Supporting Information

## Exploring the potential of the ammine complexes $M(NH_3)_n^+$ (M = Zr, Re) to activate $NH_3$

Alejandro Avilés* and Fernando Colmenares*. Departamento de Física y Química Teórica, Facultad de Química. Universidad Nacional Autónoma de México. CDMX 04510, México.

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**Table S1**. Geometrical parameters for the $M(NH_3)_n^+$ complexes.

| Complex | Spin Multiplicity | Geometry | M − N distances (Å) | N − M − N Angles (degrees) |
|---|---|---|---|---|
| $Zr(NH_3)^+$ | 4 | Linear | 2.32 | |
| $Zr(NH_3)^+$ | 2 | Linear | 2.28 | |
| $Zr(NH_3)_2^+$ | 4 | Linear | 2.36 | 179.6 |
| $Zr(NH_3)_3^+$ | 4 | Dist. trigonal | 2.40, 2.44 | 165.5, 113.8 |
| $Zr(NH_3)_4^+$ | 4 | Square planar | 2.43 | 95.0, 86.6 |
| $Zr(NH_3)_5^+$ | 4 | Square pyramid | 2.44 | 90.0 (equatorial)<br>87.1 (axial) |
| $Zr(NH_3)_6^+$ | 4 | Octahedral | 2.43 (eq.)<br>2.42 (ax.) | 86.9 (eq.)<br>89.7 (ax.) |
| $Zr(NH_3)_7^+$ | 4 | Capped octahedral | 2.49 (eq.) 2.47 (ax.) | 77.9 (eq.)<br>90.2 (ax.) |
| $Re(NH_3)^+$ | 7 | Linear | 2.46 | |
| $Re(NH_3)^+$ | 5 | Linear | 2.11 | |
| $Re(NH_3)_2^+$ | 7 | Bent | 2.47 | 91.4 |
| $Re(NH_3)_2^+$ | 5 | Linear | 2.16 | 179.7 |
| $Re(NH_3)_3^+$ | 5 | Dist. T-shaped | 2.20, 2.60 | 106.4, 82.1 |

**Table S2**. Some geometrical parameters for the located stationary points.

| | | | Distance (Å) | | | Angle (degrees) | | |
|---|---|---|---|---|---|---|---|---|
| Ion | Spin Multiplicity | Geometry | $M-N(H_3)$ | $M-N(H_2)$ | $M-H$ | $N(H_3)$-M-$N(H_3)$ | $N(H_3)$-M-$N(H_2)$ | $H-M-H$ |
| $T_1$ | 4 | Bent | | 2.50 | 1.83 | | 55.0 ($\angle H-Zr\ N$) | |
| | 2 | Bent | | 2.06 | 2.06 | | 40.0 ($\angle H-Zr\ N$) | |
| $[H-Zr-NH_2]^+$ | 4 | Bent | | 2.37 | 1.86 | | 120.5 ($\angle H-Zr\ N$) | |
| | 2 | Bent | | 1.96 | 1.85 | | 100.6 ($\angle H-Zr\ N$) | |
| $T_2$ | 4 | Dist. square pyramid | | 2.25 | 1.85, 2.00 | | 119.1, 43.0 ($\angle H-Zr\ N$) | 88.0 |
| | 2 | Dist. square pyramid | | 1.85 | 1.84, 1.92 | | 95.2, 55.0 ($\angle H-Zr\ N$) | 69.8 |
| $[(H)_2\cdots Zr-NH]^+$ | 4 | Linear | | 2.00 ($R_{Zr-NH}$) | 2.83, 2.84 | | 172.2, 171.4 ($\angle H-Zr\ N$) | 112.9 |
| $T_3$ | 4 | Dist. trigonal | | 2.56 ($R_{Zr-NH}$) | 1.97, 1.97 | | 165.4, 165.5 ($\angle H-Zr\ N$) | 29.0 |
| $[(H_2)\cdots Zr-NH]^+$ | 4 | Linear | | 2.002 ($R_{Zr-NH}$) | 2.83, 2.84 | | 172.2, 171.4 ($\angle H-Zr\ N$) | 16.3 |
| $[(H_2)\cdots Zr-NH]^+$ | 2 | Bent | | 1.81 ($R_{Zr-NH}$) | 2.37, 2.38 | | 95.5, 95.0 ($\angle H-Zr\ N$) | 19.6 |
| $Zr-NH^+$ | 4 | Linear | | 1.97 ($R_{Zr-NH}$) | | | | |
| $Zr-NH^+$ | | Linear | | 1.81 ($R_{Zr-NH}$) | | | | |
| $H-Zr(NH_3)_7^+$ | 4,2 | Square antiprismatic | 2.45 | | 1.95 | 74.04 | | |
| $[H-Zr(NH_3)_7]^+\cdots NH_2$ | 4 | - | 2.44 | 3.74 | 1.96 | 76.65 | 58.2 | |
| $TS_4$ | 4 | - | 2.49 | 2.70 | 1.97 | 74.20 | 63.1 | |
| $Zr(NH_3)_6(NH_2)^+\cdots NH_3$ | 4 | - | 2.39, 3.57 | 2.10 | 12.0 | 79.1, 62.2 | 95.1, 69.5 | |
| $Zr(NH_3)_6(NH_2)^+$ | 4 | Dist. Pentagonal Bipyramidal | 2.44 (eq.) 2.39 (ax.) | 2.092 | 12.0 | 71.8 (eq.) 168.0 (ax.) | 75.2 (eq.) 95.6 (ax.) | |
| $H_3N\cdots[H-Zr\ (NH_3)_6(NH_2)]^+$ | 2 | - | 2.45, 4.18 | 2.18 | 2.00 | 112.1, 47.2 | 77.9 | |
| $TS_4$ | 2 | - | 2.44, 4.18 | 2.14, 2.26 | 2.18, 2.15 | 73.1 | 78.2, 100.8 | 29.6 |
| $Zr(NH_3)_5(NH_2)_2^+$ | 2 | Dist. Capped octahedra | 2.45 (eq.), 2.43(ax.), 2.45 (ax.) | 2.14, 2.13 | 10.00, 9.64 | 77.6 | 81.8 | |
| $TS_5$ | 5 | Dist. See-saw | 2.19 | 2.26 | 1.81 | 172.7 | 97.4 | |
| $H-Re(NH_3)_2(NH_2)^+$ | 5 | Square planar | 2.17 | 2.04 | 1.78 | 179.4 | 90.0 | |

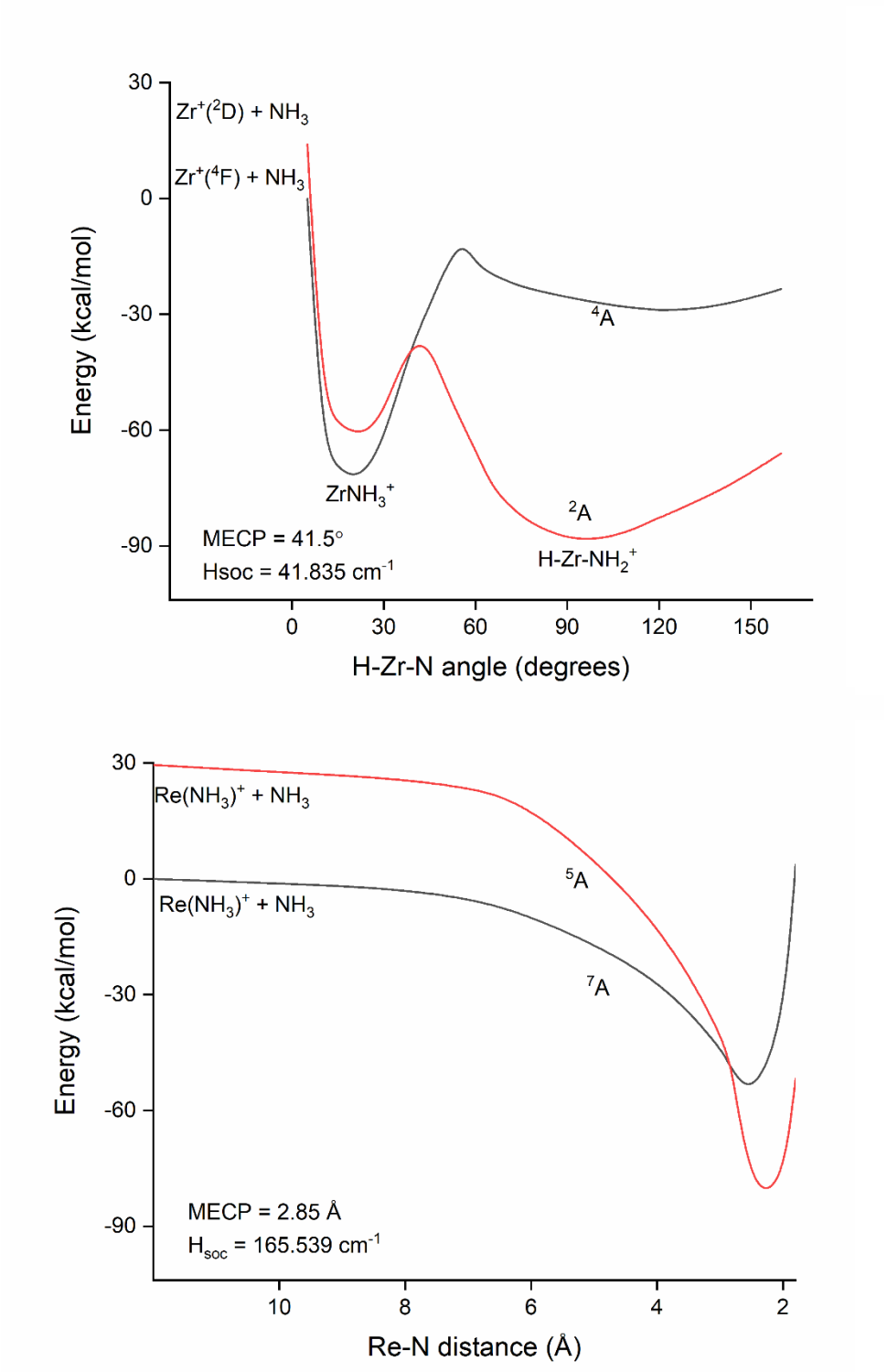


**Fig S1** Graphs showing the crossing points between electronic states of different spin multiplicity. Quartet and doublet electronic states emerging from the reactants $Zr^+ + NH_3$ (top). Septuplet and quintuplet channels that evolve from the reaction $Re(NH_3)^+ + NH_3$ (bottom).

**Table S3**. Cartesian coordinates for all the structures appearing in figures and tables.

Figure 1

Structure: $Zr(NH_3)^+$ ($^4A$)
CASPT2 Energy (Ha) = -102.60696239
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | 2.05180406 | 3.44533493 | -1.25990686 |
| N | 0.96229725 | 1.50847403 | -0.57920306 |
| H | 0.65887589 | 1.54479491 | 0.47178670 |
| H | 1.57116387 | 0.63403310 | -0.66895366 |
| H | 0.06669196 | 1.31232903 | -1.12905407 |

Structure: $Zr(NH_3)^+$ ($^2A$)
CASPT2 Energy (Ha) = -102.59772204
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | 1.99017461 | 3.46197140 | -1.22128202 |
| N | 0.96850924 | 1.51350745 | -0.59449252 |
| H | 0.61584742 | 1.47962733 | 0.44698074 |
| H | 1.58033996 | 0.60523527 | -0.70006799 |
| H | 0.06596179 | 1.29462456 | -1.18646918 |

Structure: $^4T_1$ ($^4A$)
CASPT2 Energy (Ha) = -102.51524744
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| Zr | 1.52337206 | 3.64267453 | -0.51052173 |
| N | 0.77184645 | 1.30754741 | -1.03547622 |
| H | 1.79250262 | 2.18206109 | 0.56888951 |
| H | 0.98185271 | 0.47624762 | -0.31844755 |
| H | 0.22125918 | 0.81643533 | -1.88977499 |

Structure: $^2T_1$ ($^2A$)
CASPT2 Energy (Ha) = -102.56036011
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| Zr | 1.81965940 | 3.31608563 | -0.87146013 |
| N | 1.01325934 | 1.41527016 | -0.91551147 |
| H | 0.84826716 | 1.97961857 | 0.36942821 |

| | | | |
|---|---|---|---|
| H | 1.53718991 | 0.47994470 | -0.68360103 |
| H | -0.01754277 | 1.14404694 | -1.17418655 |

Structure: H-Zr-$NH_2^+$ ($^4$A)
CASPT2 Energy (Ha) = -102.54691616
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | 1.61794017 | 3.09828922 | -0.35502113 |
| N | 0.94343712 | 1.01343007 | -1.27021968 |
| H | 1.26362214 | 3.50871878 | 1.43420916 |
| H | 1.50759161 | 0.04530470 | -1.25438672 |
| H | -0.04175803 | 0.75922322 | -1.73991259 |

Structure: H-Zr-$NH_2^+$ ($^2$A)
CASPT2 Energy (Ha) = -102.64157897
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | 1.70896337 | 2.94466686 | -0.56399838 |
| N | 1.11901013 | 1.15399734 | -1.12876874 |
| H | 0.66367963 | 3.18720373 | 0.95292757 |
| H | 1.70126182 | 0.24695832 | -1.29936768 |
| H | 0.06791808 | 0.86213977 | -1.17612376 |

Structure: $^4T_2$ ($^4$A)
CASPT2 Energy (Ha) = -102.47257930
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| Zr | 1.53914632 | 3.15136975 | -0.25741009 |
| N | 0.71009606 | 1.45931274 | -1.49551659 |
| H | 1.53960732 | 3.00101247 | 1.59525042 |
| H | 1.75390137 | 1.16438463 | -0.35026826 |
| H | 0.49808195 | 0.39888644 | -1.81996380 |

Structure: $^2T_2$ ($^2$A)
CASPT2 Energy (Ha) = -102.58901680
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| Zr | 1.72188162 | 3.34520537 | -0.46615006 |
| N | 0.85636416 | 1.75288842 | -0.85466644 |
| H | 1.87300456 | 3.01648326 | 1.34704231 |
| H | 2.45443937 | 1.58634101 | -0.16704655 |
| H | 0.43514337 | 0.77404798 | -0.94240844 |

Structure: $(H)_2$-Zr-$NH^+$ ($^4A$)
CASPT2 Energy (Ha) = -102.50842994
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | 1.71058270 | 2.22416320 | -0.00184710 |
| N | 0.21134935 | 1.18815067 | -1.64883415 |
| H | 1.10194544 | 3.40420586 | 1.29681911 |
| H | 3.43215337 | 1.59453135 | 0.34135184 |
| H | -0.49519782 | 0.68391494 | -2.39539801 |

Structure: $^4T_3$ ($^4A$)
CASPT2 Energy (Ha) = -102.45285989
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| Zr | 1.56079507 | 2.09544463 | -0.06236680 |
| N | 0.03505679 | 1.05962137 | -1.84774384 |
| H | 2.30442937 | 3.07996807 | 1.47552462 |
| H | 3.08798141 | 2.65082848 | 1.05492620 |
| H | -0.65742963 | 0.58910346 | -2.65824849 |

Structure: $(H)_2$''' Zr-$NH^+$ ($^4A$)
CASPT2 Energy (Ha) = -102.55065099
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | 1.20663675 | 1.84488404 | -0.49129038 |
| N | 0.01754263 | 1.03321467 | -1.88354613 |
| H | 2.54695074 | 3.20715484 | 1.61069930 |
| H | 3.16123098 | 2.76233531 | 1.33894986 |
| H | -0.64152810 | 0.58737714 | -2.65272094 |

Structure: $(H)_2$''' Zr-$NH^+$ ($^2A$)
CASPT2 Energy (Ha) = -102.63011207
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | 2.16119636 | 3.06968852 | -0.80252617 |
| N | 1.06198480 | 1.70519877 | -1.27677363 |
| H | 1.76508618 | 2.88019178 | 1.53237254 |
| H | 2.39228220 | 2.37598169 | 1.46267957 |
| H | 0.40028354 | 0.88390529 | -1.55898147 |

Products: Zr-$NH^+$ + $H_2$ ($^4$A)
CASPT2 Energy (Ha) = -102.54222215
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | -1.31043106 | 1.59726956 | -2.31512614 |
| N | -1.43723359 | 0.07895804 | -3.57959670 |
| H | 5.59055988 | 4.40505367 | 4.35515665 |
| H | 5.01626541 | 4.18348394 | 3.80904964 |
| H | -1.50832765 | -0.76979922 | -4.28739175 |

Products: Zr-$NH^+$ + $H_2$ ($^2$A)
CASPT2 Energy (Ha) = -102.61544212
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | 3.75689514 | 1.32946968 | -4.22219996 |
| N | 2.96509161 | 2.46022945 | -3.04366623 |
| H | -0.58668695 | 1.78240579 | 4.77380311 |
| H | -0.61549928 | 2.53482785 | 4.44146471 |
| H | 2.50103257 | 3.12277621 | -2.35263081 |

**Table 1**

Structure: $Zr(NH_3)^+$ ($^4$A)
CASPT2 Energy (Ha) = -102.60696239
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Zr | 2.05180406 | 3.44533493 | -1.25990686 |
| N | 0.96229725 | 1.50847403 | -0.57920306 |
| H | 0.65887589 | 1.54479491 | 0.47178670 |
| H | 1.57116387 | 0.63403310 | -0.66895366 |
| H | 0.06669196 | 1.31232903 | -1.12905407 |

Structure: $Zr(NH_3)_2^+$ ($^4$A)
CASPT2 Energy (Ha) = -158.87181581
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 1.01468989 | 5.51582230 | -1.43005604 |
| Zr | 3.15494584 | 5.79687209 | -0.47318472 |
| N | 5.29157868 | 6.07606639 | 0.49600254 |
| H | 0.22743215 | 5.35300157 | -0.68548593 |
| H | 0.93904488 | 4.64452447 | -2.09031604 |

| | | | |
|---|---|---|---|
| H | 0.69748404 | 6.35252085 | -2.01306265 |
| H | 6.06027657 | 6.20054206 | -0.23325494 |
| H | 5.34695529 | 6.91562695 | 1.15219538 |
| H | 5.58335066 | 5.20968232 | 1.09348941 |

Structure: $Zr(NH_3)_3^+$ ($^4A$)
CASPT2 Energy (Ha) = -215.10714720
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 1.63247643 | 5.42315710 | -1.80679152 |
| Zr | 3.19495721 | 7.20247664 | -2.42602182 |
| N | 2.48345178 | 9.37233056 | -1.77877457 |
| H | 1.93809364 | 4.43470885 | -2.05495550 |
| H | 0.69003901 | 5.57981158 | -2.27690282 |
| H | 1.46168856 | 5.43789237 | -0.75611100 |
| H | 3.20976894 | 10.07837639 | -2.10765102 |
| H | 1.55435111 | 9.65677176 | -2.21404926 |
| H | 2.38999230 | 9.48894722 | -0.72467550 |
| N | 4.43348058 | 5.29340254 | -3.20232376 |
| H | 4.60819472 | 5.38477301 | -4.27891257 |
| H | 5.40221311 | 5.31847183 | -2.75750867 |
| H | 4.06975060 | 4.26869008 | -3.07409094 |

Structure: $Zr(NH_3)_4^+$ ($^4A$)
CASPT2 Energy (Ha) = -271.34419507
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 1.58609074 | 7.02433046 | -1.52337387 |
| N | 4.79101712 | 6.42196229 | -0.84017244 |
| Zr | 3.67410209 | 7.89633878 | -2.41098146 |
| N | 2.52339026 | 9.36657426 | -3.96571782 |
| H | 1.71153584 | 6.04806502 | -1.12413529 |
| H | 0.83404083 | 6.95012211 | -2.27087717 |
| H | 1.21540133 | 7.65177382 | -0.74975488 |
| H | 2.91770168 | 9.33598494 | -4.95249024 |
| H | 1.49386874 | 9.11567548 | -4.03736977 |
| H | 2.57542953 | 10.36875324 | -3.61469622 |
| H | 4.86506035 | 5.39925389 | -1.21087505 |
| H | 5.78831561 | 6.74209940 | -0.65510752 |
| H | 4.30747132 | 6.37920803 | 0.10670682 |
| N | 5.71951476 | 8.77237125 | -3.37256060 |
| H | 5.66291856 | 9.80456531 | -3.63025442 |
| H | 6.57859919 | 8.69058319 | -2.70106315 |
| H | 6.03118298 | 8.23698159 | -4.27451888 |

Structure: $Zr(NH_3)_5^+$ ($^4A$)
CASPT2 Energy (Ha) = -327.56458158
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 4.39338598 | 7.35842739 | -0.35330819 |
| N | 2.05459071 | 7.31234710 | -2.82023200 |
| Zr | 4.08928339 | 8.62737235 | -2.46572784 |
| N | 6.21485417 | 9.72521070 | -2.00815191 |
| N | 5.40940159 | 6.88014192 | -3.54878482 |
| H | 3.72150430 | 7.67537572 | 0.40549011 |
| H | 5.37932341 | 7.45193838 | 0.02990262 |
| H | 4.21649891 | 6.32383863 | -0.51877685 |
| H | 6.39350191 | 6.57206328 | -3.16765176 |
| H | 4.91576080 | 5.93544323 | -3.80645865 |
| H | 5.60996525 | 7.33823252 | -4.52002054 |
| H | 1.32223137 | 7.25929702 | -2.05062311 |
| H | 1.66300140 | 7.88920584 | -3.61792863 |
| H | 2.19506219 | 6.32840790 | -3.19369926 |
| H | 6.06175800 | 10.70962298 | -2.37308261 |
| H | 6.58147407 | 9.80044637 | -1.01184861 |
| H | 6.98476805 | 9.31051140 | -2.60880973 |
| N | 2.69017759 | 10.19763530 | -1.23215120 |
| H | 2.94949401 | 11.13963189 | -1.64568126 |
| H | 1.66777433 | 10.04812666 | -1.47278104 |
| H | 2.77034361 | 10.27333238 | -0.17353165 |

Structure: $Zr(NH_3)_6^+$ ($^4A$)
CASPT2 Energy (Ha) = -383.78393333
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 3.34330609 | 9.78986722 | -2.15067442 |
| Zr | 5.23816138 | 8.26077785 | -2.26492375 |
| N | 6.87010771 | 10.06329068 | -2.15031546 |
| N | 3.60564225 | 6.45536970 | -2.38445945 |
| N | 5.26169476 | 8.41050285 | -4.68659067 |
| N | 5.21164128 | 8.10944030 | 0.15654145 |
| H | 2.73501957 | 9.61121060 | -1.29643539 |
| H | 2.69940821 | 9.71772819 | -2.99479496 |
| H | 3.66157310 | 10.80278461 | -2.09661459 |
| H | 7.46672466 | 10.02721711 | -1.26817054 |
| H | 7.55145407 | 10.06772192 | -2.96912939 |
| H | 6.40727870 | 11.05058464 | -2.14733822 |
| H | 5.74067159 | 7.58315587 | -5.15316454 |
| H | 4.26751520 | 8.43325300 | -5.06659773 |
| H | 5.73715975 | 9.29258448 | -5.04379178 |
| H | 4.71018753 | 7.24008901 | 0.50924199 |

| | | | |
|---|---|---|---|
| H | 6.20708496 | 8.04872569 | 0.52923323 |
| H | 4.76311804 | 8.94784598 | 0.63356640 |
| H | 2.93811162 | 6.44737794 | -1.55568948 |
| H | 2.99771757 | 6.51497781 | -3.25604754 |
| H | 4.07709846 | 5.50237628 | -2.40918348 |
| N | 7.13251178 | 6.73273846 | -2.37344962 |
| H | 7.78829668 | 6.82315738 | -1.53969752 |
| H | 6.81844616 | 5.71709053 | -2.40309390 |
| H | 7.73021495 | 6.89448698 | -3.23907572 |

Structure: $Zr(NH_3)_7^+$ ($^4A$)
CASPT2 Energy (Ha) = -440.01085281
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 6.61467572 | 9.88696069 | -3.15633540 |
| Zr | 4.31345952 | 9.01960269 | -3.39824066 |
| N | 4.65407290 | 9.95533217 | -5.67111251 |
| N | 4.07243783 | 8.94887699 | -0.94682596 |
| N | 1.83294042 | 8.87583790 | -3.30438133 |
| N | 5.65106492 | 6.99941993 | -2.80020259 |
| N | 3.70291399 | 11.36896699 | -3.01938669 |
| H | 7.28491921 | 9.24819752 | -3.67546247 |
| H | 6.96149107 | 9.94639883 | -2.15230901 |
| H | 6.73747738 | 10.85429607 | -3.57842619 |
| H | 3.79078327 | 9.95861813 | -6.29370454 |
| H | 4.99210612 | 10.99034755 | -5.64051161 |
| H | 5.41129279 | 9.42765523 | -6.19974007 |
| H | 1.52004727 | 7.89441822 | -3.04704811 |
| H | 1.42306973 | 9.53021438 | -2.57534939 |
| H | 1.36431702 | 9.12015278 | -4.22632352 |
| H | 6.34486231 | 7.21129999 | -2.02496181 |
| H | 5.04334911 | 6.19559727 | -2.46303646 |
| H | 6.21471379 | 6.63611700 | -3.62359854 |
| H | 4.37671042 | 8.02131770 | -0.53159434 |
| H | 4.65491548 | 9.70280278 | -0.47355146 |
| H | 3.06766516 | 9.10096088 | -0.63911298 |
| H | 3.03617023 | 11.72686365 | -3.80795019 |
| H | 3.14251211 | 11.56539662 | -2.10119944 |
| H | 4.51791206 | 12.05509037 | -3.00268007 |
| N | 3.68351414 | 7.20949914 | -4.99090761 |
| H | 4.50617801 | 6.91381635 | -5.59349409 |
| H | 3.33057086 | 6.33789261 | -4.49768730 |
| H | 2.91556615 | 7.52089562 | -5.65380365 |

**Figure 2**

Reactants: $Zr(NH_3)_7^+ + NH_3 (^4A)$
CASPT2 Energy (Ha) = -496.14548141
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 2.63603118 | 10.31230706 | -2.09260249 |
| Zr | 4.27951462 | 9.04125461 | -3.46843458 |
| N | 6.67227447 | 9.27824203 | -2.79074542 |
| N | 4.84329340 | 11.35121136 | -4.14716262 |
| N | 3.42784629 | 6.69790680 | -3.52865949 |
| N | 5.48125355 | 8.20037498 | -5.45626294 |
| N | 4.49063655 | 8.16021145 | -1.14342817 |
| N | 2.38613677 | 9.27552857 | -5.03363100 |
| H | 3.08872084 | 10.71576366 | -1.22095340 |
| H | 1.81342190 | 9.72182581 | -1.76880972 |
| H | 2.23068936 | 11.13250544 | -2.63139287 |
| H | 5.03110209 | 11.92310513 | -3.27264640 |
| H | 5.71603198 | 11.42034636 | -4.74976548 |
| H | 4.06834903 | 11.84876984 | -4.67830662 |
| H | 6.34535113 | 7.66659586 | -5.14905072 |
| H | 4.90553436 | 7.52843084 | -6.04411404 |
| H | 5.81073516 | 8.97351228 | -6.10857506 |
| H | 3.55214542 | 7.85697853 | -0.75076153 |
| H | 5.13345450 | 7.31636447 | -1.09449833 |
| H | 4.88401893 | 8.88659752 | -0.47607451 |
| H | 4.20732270 | 6.01775037 | -3.28826450 |
| H | 2.63396720 | 6.51237545 | -2.84703277 |
| H | 3.07323545 | 6.42622103 | -4.49215470 |
| H | 1.55438290 | 8.74396211 | -4.64313674 |
| H | 2.06541761 | 10.27794641 | -5.17902696 |
| H | 2.58409950 | 8.87637129 | -5.99846456 |
| H | 6.78280899 | 9.95184952 | -1.97641890 |
| H | 7.11055829 | 8.35765724 | -2.49084533 |
| H | 7.26975061 | 9.65823059 | -3.58222497 |
| N | -7.28443949 | 7.83703706 | -6.43909537 |
| H | -7.71991351 | 8.81777435 | -6.57540840 |
| H | -7.36593336 | 7.27194514 | -7.35783936 |
| H | -7.80208240 | 7.31639684 | -5.64470907 |

Radical fragments: $[H\text{-}Zr(NH_3)_7]^+ + NH_2 (^4A)$
CASPT2 Energy (Ha) = -496.14420445
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 2.72991997 | 10.16009135 | -2.30235656 |
| Zr | 4.39721192 | 9.02836639 | -3.70858342 |

| | | | |
|---|---|---|---|
| N | 5.70775955 | 9.59482167 | -1.71922088 |
| N | 3.54503954 | 7.11057934 | -4.96737713 |
| N | 3.62696596 | 7.34707213 | -2.09124888 |
| N | 5.11993674 | 11.33009290 | -4.01738289 |
| N | 6.32936655 | 7.55248475 | -3.73630801 |
| N | 2.64559337 | 9.90245888 | -5.17769283 |
| N | 8.75513011 | 18.71552390 | 1.87420510 |
| H | 1.77193956 | 9.71887659 | -2.45937905 |
| H | 2.57161625 | 11.22930999 | -2.45486361 |
| H | 2.89854753 | 10.05988617 | -1.25442697 |
| H | 2.59725574 | 7.12832198 | -2.26363020 |
| H | 4.11990060 | 6.37296129 | -2.09290763 |
| H | 3.66300255 | 7.66260000 | -1.07318095 |
| H | 6.31957107 | 7.09868618 | -4.68977137 |
| H | 7.20121539 | 8.15151081 | -3.71775464 |
| H | 6.44639461 | 6.79368513 | -3.00301584 |
| H | 2.44642004 | 10.93484646 | -5.04586800 |
| H | 2.96844771 | 9.76790786 | -6.17612552 |
| H | 1.71459386 | 9.40643459 | -5.06317059 |
| H | 4.87456020 | 11.57233004 | -5.01556875 |
| H | 4.76294621 | 12.10452146 | -3.38488794 |
| H | 6.17685747 | 11.34544304 | -3.97552248 |
| H | 5.27418072 | 10.38152894 | -1.15375304 |
| H | 5.80197471 | 8.77432436 | -1.05255514 |
| H | 6.69638490 | 9.90511571 | -1.95280861 |
| H | 2.49575977 | 6.98164973 | -4.87589071 |
| H | 3.76861548 | 7.26632715 | -5.98976950 |
| H | 3.97895032 | 6.18565533 | -4.68611161 |
| H | 8.31421947 | 19.15886691 | 2.80449790 |
| H | 9.64009766 | 19.37406770 | 1.67540778 |
| H | 5.24966748 | 9.17288726 | -5.46428802 |

Radical fragments: $[H\text{-}Zr(NH_3)_7]^+$ + $NH_2$ ($^2A$)
CASPT2 Energy (Ha) = -496.14433227
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 2.72991997 | 10.16009135 | -2.30235656 |
| Zr | 4.39721192 | 9.02836639 | -3.70858342 |
| N | 5.70775955 | 9.59482167 | -1.71922088 |
| N | 3.54503954 | 7.11057934 | -4.96737713 |
| N | 3.62696596 | 7.34707213 | -2.09124888 |
| N | 5.11993674 | 11.33009290 | -4.01738289 |
| N | 6.32936655 | 7.55248475 | -3.73630801 |
| N | 2.64559337 | 9.90245888 | -5.17769283 |
| N | 8.75513011 | 18.71552390 | 1.87420510 |
| H | 1.77193956 | 9.71887659 | -2.45937905 |
| H | 2.57161625 | 11.22930999 | -2.45486361 |
| H | 2.89854753 | 10.05988617 | -1.25442697 |

| | | | |
|---|---|---|---|
| H | 2.59725574 | 7.12832198 | -2.26363020 |
| H | 4.11990060 | 6.37296129 | -2.09290763 |
| H | 3.66300255 | 7.66260000 | -1.07318095 |
| H | 6.31957107 | 7.09868618 | -4.68977137 |
| H | 7.20121539 | 8.15151081 | -3.71775464 |
| H | 6.44639461 | 6.79368513 | -3.00301584 |
| H | 2.44642004 | 10.93484646 | -5.04586800 |
| H | 2.96844771 | 9.76790786 | -6.17612552 |
| H | 1.71459386 | 9.40643459 | -5.06317059 |
| H | 4.87456020 | 11.57233004 | -5.01556875 |
| H | 4.76294621 | 12.10452146 | -3.38488794 |
| H | 6.17685747 | 11.34544304 | -3.97552248 |
| H | 5.27418072 | 10.38152894 | -1.15375304 |
| H | 5.80197471 | 8.77432436 | -1.05255514 |
| H | 6.69638490 | 9.90511571 | -1.95280861 |
| H | 2.49575977 | 6.98164973 | -4.87589071 |
| H | 3.76861548 | 7.26632715 | -5.98976950 |
| H | 3.97895032 | 6.18565533 | -4.68611161 |
| H | 8.31421947 | 19.15886691 | 2.80449790 |
| H | 9.64009766 | 19.37406770 | 1.67540778 |
| H | 5.24966748 | 9.17288726 | -5.46428802 |

Structure: $[H\text{-}Zr(NH_3)_7]^+ \cdots NH_2$ ($^4A$)
CASPT2 Energy (Ha) = -496.17582476
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 3.83230967 | 11.22940009 | -1.40667637 |
| Zr | 4.73941098 | 9.72535835 | -3.08848303 |
| N | 5.10692859 | 8.40742277 | -1.03907773 |
| N | 4.09211540 | 8.37719307 | -5.02067889 |
| N | 2.61386508 | 8.60735783 | -2.53720255 |
| N | 6.66094153 | 10.85730627 | -2.11393345 |
| N | 6.58288236 | 8.18184201 | -3.52248960 |
| N | 3.12701709 | 11.13119407 | -4.25174201 |
| N | 5.27252266 | 13.40598323 | -3.50372336 |
| H | 4.06535807 | 12.22858596 | -1.67615263 |
| H | 4.24210351 | 11.07779745 | -0.41313092 |
| H | 2.78057403 | 11.16869914 | -1.28742518 |
| H | 1.75516199 | 8.78963373 | -3.14108036 |
| H | 2.76422193 | 7.52877256 | -2.60481021 |
| H | 2.29101213 | 8.74688873 | -1.53080054 |
| H | 6.97210947 | 8.39249743 | -4.48382345 |
| H | 7.38894666 | 8.25037504 | -2.83800019 |
| H | 6.27652715 | 7.16587665 | -3.50845576 |
| H | 3.18186802 | 12.12467516 | -3.89685326 |
| H | 3.47919309 | 11.14719726 | -5.24598041 |
| H | 2.10322747 | 10.85609445 | -4.26499912 |
| H | 6.43190425 | 11.87273012 | -1.93473071 |

| | | | |
|---|---|---|---|
| H | 7.10438220 | 10.47226607 | -1.23132611 |
| H | 7.38324927 | 10.84266254 | -2.88265946 |
| H | 4.42854893 | 8.63438972 | -0.25019810 |
| H | 4.91743516 | 7.38395903 | -1.26658173 |
| H | 6.07497228 | 8.42137172 | -0.59760522 |
| H | 3.11625392 | 8.56906141 | -5.38641452 |
| H | 4.76724832 | 8.57918224 | -5.81036461 |
| H | 4.12601966 | 7.33580423 | -4.81945480 |
| H | 5.52279215 | 14.44148599 | -3.78310534 |
| H | 5.69891667 | 12.77953458 | -4.28597041 |
| H | 5.71002333 | 10.55663712 | -4.58737991 |

Transition state: $^4T_4$ ($^4A$)
CASPT2 Energy (Ha) = -496.14544820
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| N | 4.16629088 | 10.93398681 | -0.97311945 |
| Zr | 4.80910726 | 9.91179423 | -3.11455438 |
| N | 3.72662079 | 8.09739689 | -1.78142961 |
| N | 4.10401165 | 9.81572609 | -5.48962968 |
| N | 2.33413993 | 10.20330635 | -3.24431650 |
| N | 6.62389889 | 9.05872591 | -1.63691813 |
| N | 5.45078934 | 7.71376639 | -4.03846145 |
| N | 4.49842430 | 12.26308894 | -3.85471239 |
| N | 6.61106155 | 11.71783780 | -2.23071777 |
| H | 4.70480322 | 11.82769718 | -0.80577139 |
| H | 4.41154369 | 10.28420483 | -0.13758289 |
| H | 3.13541459 | 11.15653830 | -0.85109137 |
| H | 1.92731022 | 11.12995037 | -3.57901697 |
| H | 1.91921952 | 9.45861474 | -3.92402004 |
| H | 1.83143235 | 9.99495503 | -2.32853651 |
| H | 6.11535070 | 7.91238257 | -4.83563676 |
| H | 5.95672311 | 7.06720842 | -3.36927634 |
| H | 4.63157501 | 7.15677623 | -4.41877860 |
| H | 4.50482457 | 12.95684201 | -3.05624474 |
| H | 5.33334143 | 12.46769610 | -4.46919671 |
| H | 3.62722806 | 12.45782308 | -4.42432052 |
| H | 6.79533721 | 9.66135161 | -0.78484464 |
| H | 6.51424469 | 8.06357943 | -1.29143137 |
| H | 7.49255836 | 9.09474808 | -2.23809820 |
| H | 3.08654279 | 8.44006744 | -1.00275535 |
| H | 3.08138093 | 7.55929665 | -2.43570305 |
| H | 4.34444706 | 7.35970130 | -1.32801857 |
| H | 3.47549909 | 10.60225154 | -5.81866933 |
| H | 4.99223307 | 9.86029788 | -6.06074210 |
| H | 3.59787738 | 8.91695551 | -5.73773302 |
| H | 7.12859174 | 12.50240988 | -1.66860290 |
| H | 7.27098903 | 11.47128711 | -3.03764969 |

| | | | |
|---|---|---|---|
| H | 6.40723072 | 10.17097134 | -4.24372957 |

Structure: $Zr(NH_3)_6(NH_2)^+ \cdots NH_3 + H$ ($^4A$)
CASPT2 Energy (Ha) = -496.18487689
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 3.34364659 | 11.09581533 | -1.44881562 |
| Zr | 4.91538616 | 9.67674586 | -2.57373480 |
| N | 4.75023329 | 8.32834095 | -0.52820254 |
| N | 4.59601007 | 8.89683791 | -4.86668445 |
| N | 2.82289246 | 8.44060393 | -2.70531592 |
| N | 6.36746060 | 10.82436299 | -1.02117894 |
| N | 6.64800490 | 8.04466227 | -2.87375059 |
| N | 2.35318627 | 11.21916051 | -4.54101114 |
| N | 5.72596589 | 11.20446780 | -3.76967349 |
| H | 2.32195767 | 10.95261499 | -1.69078780 |
| H | 3.58562239 | 12.10977141 | -1.74926537 |
| H | 3.41149125 | 11.08070120 | -0.38801535 |
| H | 2.19116955 | 8.91718121 | -3.41149214 |
| H | 2.91285932 | 7.40049026 | -3.01043170 |
| H | 2.29702002 | 8.40020354 | -1.78351460 |
| H | 7.29278229 | 8.34702021 | -3.66143219 |
| H | 7.24804409 | 7.94353960 | -2.00454502 |
| H | 6.30612268 | 7.06506089 | -3.10175766 |
| H | 1.55090370 | 11.72787453 | -4.04672958 |
| H | 3.24719718 | 11.76427182 | -4.37946272 |
| H | 2.12755393 | 11.23865751 | -5.58927235 |
| H | 6.18572170 | 10.61914105 | 0.00411019 |
| H | 7.37878756 | 10.56060099 | -1.20623562 |
| H | 6.30551905 | 11.87699991 | -1.13863134 |
| H | 3.99950696 | 8.61538352 | 0.17792918 |
| H | 4.52475199 | 7.31384658 | -0.77100880 |
| H | 5.65237337 | 8.27587821 | 0.03713321 |
| H | 3.74395587 | 9.38350506 | -5.25733192 |
| H | 5.42432178 | 9.16224553 | -5.46897055 |
| H | 4.44950311 | 7.85327076 | -4.97567737 |
| H | 6.32753144 | 11.99802119 | -3.44168609 |
| H | 5.69351576 | 11.31443981 | -4.83722909 |
| H | 8.98904412 | 15.71751867 | -12.10863784 |

Products: $Zr(NH_3)_6(NH_2)^+ + NH_3 + H$ ($^4A$)
CASPT2 Energy (Ha) = -496.14634031
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 3.74454799 | 11.93807035 | -0.58782053 |
| Zr | 5.32302999 | 10.62773235 | -1.81054393 |

| | | | |
|---|---|---|---|
| N | 6.10256804 | 9.48955414 | 0.21718437 |
| N | 4.01723925 | 10.04781419 | -3.80346774 |
| N | 3.67206390 | 8.92171943 | -1.17184304 |
| N | 6.85940852 | 12.12645559 | -0.64039496 |
| N | 6.76656060 | 8.95055504 | -2.72590443 |
| N | -0.41556338 | 4.40776885 | -10.31822282 |
| N | 5.80251489 | 12.10336076 | -3.21482890 |
| H | 2.73006631 | 11.65163329 | -0.72236957 |
| H | 3.81849777 | 12.95505154 | -0.96440435 |
| H | 3.89513596 | 11.99763555 | 0.46375797 |
| H | 2.71227022 | 9.03407473 | -1.62103917 |
| H | 3.96113950 | 7.88617825 | -1.37280426 |
| H | 3.49447930 | 8.93986102 | -0.12027450 |
| H | 7.13602598 | 9.35636270 | -3.63220810 |
| H | 7.60759042 | 8.73680078 | -2.11580390 |
| H | 6.31731802 | 8.01535800 | -2.95366320 |
| H | -1.04517092 | 3.68619078 | -9.81513326 |
| H | -1.02662983 | 5.06158210 | -10.92593888 |
| H | 0.29879221 | 3.89157284 | -10.94541390 |
| H | 6.80954015 | 12.07134662 | 0.41736102 |
| H | 7.87155767 | 11.95139829 | -0.91189336 |
| H | 6.63620097 | 13.12740361 | -0.90743197 |
| H | 5.57858943 | 9.77712321 | 1.10249872 |
| H | 5.97420149 | 8.43332038 | 0.15529221 |
| H | 7.13547327 | 9.63759314 | 0.43004861 |
| H | 3.17653131 | 10.68982123 | -3.90105450 |
| H | 4.61121926 | 10.18660422 | -4.67005829 |
| H | 3.65263421 | 9.05285400 | -3.83672243 |
| H | 6.55392345 | 12.82819185 | -3.13081806 |
| H | 5.40187565 | 12.21552722 | -4.17607413 |
| H | 9.71641139 | 17.77271993 | -9.72132073 |

Structure: $H_3N\cdots[H\text{-}Zr(NH_3)_6(NH_2)]^+$ ($^2A$)
CASPT2 Energy (Ha) = -496.2728640
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 3.49960286 | 10.96052408 | -1.71526359 |
| Zr | 4.69628839 | 9.55783638 | -3.36532121 |
| N | 6.17779743 | 9.62895477 | -1.75433028 |
| N | 3.09632532 | 8.00799708 | -4.54376243 |
| N | 3.75444414 | 7.93735701 | -1.72300159 |
| N | 5.83749161 | 11.63026191 | -3.93038847 |
| N | 6.07201773 | 7.58346761 | -3.84546129 |
| N | 3.01323146 | 11.00110224 | -4.56338068 |
| N | 5.93192463 | 12.83264207 | -1.07631055 |
| H | 2.43978383 | 10.97377246 | -1.73873674 |
| H | 3.84078150 | 11.98594991 | -1.78936693 |
| H | 3.80029812 | 10.64441834 | -0.75375320 |

| | | | |
|---|---|---|---|
| H | 2.69988748 | 7.90256047 | -1.60745003 |
| H | 4.07134776 | 6.93037939 | -1.97070433 |
| H | 4.18792240 | 8.14930341 | -0.78190112 |
| H | 5.78853879 | 6.94633995 | -4.64121229 |
| H | 6.92046246 | 8.11241993 | -4.17297684 |
| H | 6.35370140 | 7.00659987 | -3.00466995 |
| H | 3.13190625 | 12.02508701 | -4.32604680 |
| H | 3.29875780 | 10.86476630 | -5.56964207 |
| H | 1.98301469 | 10.76781825 | -4.46740507 |
| H | 5.74831956 | 11.82769652 | -4.96083245 |
| H | 5.62727014 | 12.50158077 | -3.36716883 |
| H | 6.84096072 | 11.37014018 | -3.74912016 |
| H | 6.20733094 | 11.80643650 | -1.16129544 |
| H | 6.05399197 | 9.42839130 | -0.72808579 |
| H | 7.21473502 | 9.57832078 | -1.91484539 |
| H | 2.05579961 | 8.17897956 | -4.42985830 |
| H | 3.37005703 | 8.21421809 | -5.54049572 |
| H | 3.27153864 | 6.97952080 | -4.36739379 |
| H | 6.79278958 | 13.44380306 | -1.28288146 |
| H | 5.66509985 | 13.02777015 | -0.02368826 |
| H | 5.20662399 | 9.52281990 | -5.30455896 |

Transition state: $^2T_3$ ($^2A$)
CASPT2 Energy (Ha) = -496.23481245
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| N | 4.09097605 | 10.11299440 | -1.11234717 |
| Zr | 4.54342676 | 9.04556366 | -3.08158967 |
| N | 2.39813430 | 7.97143257 | -2.58528741 |
| N | 6.48184768 | 7.64667727 | -3.81200939 |
| N | 2.92988000 | 10.33161918 | -3.97699570 |
| N | 5.70431842 | 10.43716604 | -4.66089402 |
| N | 4.98121740 | 7.36480630 | -1.29719786 |
| N | 3.91204370 | 7.96241095 | -5.23090277 |
| H | 3.97179421 | 9.73455835 | -0.13497164 |
| H | 3.71254549 | 11.09147516 | -1.11824694 |
| H | 5.39289410 | 10.10978326 | -1.42451812 |
| H | 6.76902525 | 7.86736541 | -4.80558293 |
| H | 7.29212223 | 7.89839603 | -3.18140492 |
| H | 6.32350333 | 6.60031397 | -3.75724554 |
| H | 6.72482292 | 10.25008740 | -4.86095884 |
| H | 5.19817552 | 10.54234530 | -5.58160489 |
| H | 5.65193556 | 11.36721955 | -4.15501115 |
| H | 4.25203753 | 7.43112446 | -0.53239188 |
| H | 4.99426808 | 6.32522976 | -1.61504920 |
| H | 5.92154300 | 7.56387633 | -0.85206741 |
| H | 2.12191790 | 10.58679360 | -3.29537965 |
| H | 3.14595860 | 8.65601018 | -5.44021287 |

| | | | |
|---|---|---|---|
| H | 3.22253655 | 11.31919435 | -4.32096283 |
| H | 4.60923490 | 7.98107791 | -6.02713306 |
| H | 3.50105643 | 6.98697904 | -5.19280731 |
| H | 2.30309851 | 6.92026116 | -2.48962128 |
| H | 2.04249468 | 8.42228697 | -1.69881787 |
| H | 1.77667131 | 8.29797632 | -3.37239569 |
| H | 6.24081433 | 9.78500574 | -2.03356738 |
| N | 5.42624132 | 12.84565391 | -2.82599949 |
| H | 4.40284746 | 13.03534429 | -2.58263161 |
| H | 5.93076185 | 12.49953674 | -1.95061652 |
| H | 5.87978166 | 13.76258846 | -3.15425207 |

Structure: $H_3N \cdots Zr(NH_3)_5(NH_2)_2^+ \cdots H_2$ ($^2A$)
CASPT2 Energy (Ha) = -496.28723511
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 4.05654679 | 9.92116581 | -1.24173854 |
| Zr | 4.05904559 | 9.05321688 | -3.16544779 |
| N | 2.30545716 | 7.77548206 | -2.00516612 |
| N | 6.50244919 | 9.32788416 | -3.33525291 |
| N | 2.25641929 | 9.58656013 | -4.31041752 |
| N | 4.45412339 | 11.21153522 | -4.22344327 |
| N | 5.02487163 | 6.88605012 | -2.53961030 |
| N | 4.44811297 | 7.92919359 | -5.40269286 |
| H | 3.46752599 | 9.64932821 | -0.41510976 |
| H | 4.60295646 | 10.76760210 | -0.95326074 |
| H | 6.60036212 | 8.74620493 | -0.06745183 |
| H | 6.89548606 | 9.35478577 | -4.31759825 |
| H | 6.64675684 | 10.27805486 | -2.89288160 |
| H | 7.07943474 | 8.63603165 | -2.78322110 |
| H | 5.40223525 | 11.67836070 | -4.19530736 |
| H | 4.10579021 | 11.17772931 | -5.21977076 |
| H | 3.78274755 | 11.81646608 | -3.67861830 |
| H | 4.30946213 | 6.11089791 | -2.60385776 |
| H | 5.84678533 | 6.61438374 | -3.14650246 |
| H | 5.35338027 | 6.94404909 | -1.53476167 |
| H | 1.37816838 | 8.95008190 | -4.30751166 |
| H | 3.58211771 | 8.40935028 | -5.76152210 |
| H | 1.81656234 | 10.57769183 | -4.29381513 |
| H | 5.26718063 | 8.19189786 | -6.02462939 |
| H | 4.30690288 | 6.88167634 | -5.49042604 |
| H | 2.55961065 | 7.32449850 | -1.07986351 |
| H | 1.66056480 | 8.58429604 | -1.80477003 |
| H | 1.76329340 | 7.07246727 | -2.58421473 |
| H | 7.28061166 | 8.41122176 | 0.10521916 |
| N | 6.68649793 | 12.11913316 | -1.88357055 |
| H | 6.95730734 | 11.69345915 | -0.93531188 |
| H | 7.49655209 | 12.75321638 | -2.20665084 |

| | | | |
|---|---|---|---|
| H | 5.82158923 | 12.73450104 | -1.72866210 |

Products: $Zr(NH_3)_5(NH_2)_2^+ + H_2 + NH_3$ ($^2A$)
CASPT2 Energy (Ha) = -496.25631518
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 4.93706099 | 11.58697043 | -2.46039388 |
| Zr | 3.20523031 | 10.52099803 | -3.15197015 |
| N | 2.81945842 | 12.62688060 | -4.31442678 |
| N | 4.62856806 | 8.50473593 | -3.01551092 |
| N | 3.15477932 | 9.78864875 | -0.82224606 |
| N | 4.39286597 | 10.38080582 | -5.31690775 |
| N | 1.31716019 | 11.18316531 | -2.42401857 |
| N | 1.89175767 | 8.81452086 | -4.41440332 |
| N | 3.87639697 | 6.28277438 | -14.35853037 |
| H | 5.45966826 | 11.43145878 | -1.53051775 |
| H | 5.31925534 | 12.50078772 | -2.81428610 |
| H | 9.83534028 | 0.53626197 | -2.56316940 |
| H | 3.94859144 | 10.95479037 | -6.08686639 |
| H | 5.32120675 | 10.81871957 | -5.06516248 |
| H | 4.57969555 | 9.41748948 | -5.71511340 |
| H | 3.66413645 | 13.05383093 | -4.79483064 |
| H | 1.96712594 | 12.76258281 | -4.98444464 |
| H | 2.60876767 | 13.26993190 | -3.46663385 |
| H | 4.34217426 | 7.83308190 | -2.24994067 |
| H | 4.76390145 | 7.93418736 | -3.89726419 |
| H | 5.55819340 | 8.93421388 | -2.75435744 |
| H | 0.83186326 | 10.86102128 | -1.55156231 |
| H | 0.96306261 | 9.16034726 | -4.05858769 |
| H | 0.70765794 | 11.92102313 | -2.85317836 |
| H | 1.87627633 | 8.86180812 | -5.47428192 |
| H | 1.98936827 | 7.79454341 | -4.13909710 |
| H | 4.08602873 | 9.47110964 | -0.43142489 |
| H | 2.94656580 | 10.73024215 | -0.39483638 |
| H | 2.40639581 | 9.10943568 | -0.49809415 |
| H | 10.44625721 | 1.03641833 | -2.48141365 |
| H | 3.73168022 | 5.21071480 | -14.36396822 |
| H | 3.09697190 | 6.75678507 | -14.93998628 |
| H | 4.84202719 | 6.52048934 | -14.78437731 |

**Figure 3**

(left)

Reactants: $Re^+ + NH_3$ ($^7A$)
CASPT2 Energy (Ha) = -133.54649873
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Re | 5.51776201 | 9.80714644 | -3.90204296 |
| N | 0.03823256 | -0.13350044 | -0.00867725 |
| H | -0.18539223 | 0.04138905 | 1.07505498 |
| H | 0.66720284 | -1.05999138 | -0.02494414 |
| H | -0.90697218 | -0.39007767 | -0.48472160 |

Structure: $Re(NH_3)^+$ ($^7A$)
CASPT2 Energy (Ha) = -133.63972394
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Re | 2.03917506 | 3.53460723 | -1.30957988 |
| N | 0.91262160 | 1.46028026 | -0.61134175 |
| H | 0.61445809 | 1.45862171 | 0.44668397 |
| H | 1.54406093 | 0.56563255 | -0.70681195 |
| H | 0.02051730 | 1.24582425 | -1.16428137 |

Transition state: TS ($^7A$)
CASPT2 Energy (Ha) = -133.51521496
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| Re | 1.55910000 | 3.92540000 | -0.41740000 |
| N | 0.66550000 | 1.09060000 | -1.08340000 |
| H | 1.82300000 | 2.44860000 | 0.35320000 |
| H | 1.01240000 | 0.30110000 | -0.34930000 |
| H | 0.09080000 | 0.51910000 | -1.82850000 |

Structure: H-Re-$NH_2^+$ ($^7A$)
CASPT2 Energy (Ha) = -133.51521563
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Re | 1.20734843 | 2.89349816 | -0.04141772 |
| N | 0.92409752 | 0.74798221 | -1.09546339 |
| H | 1.39475966 | 4.43073378 | 0.70604686 |
| H | 1.68581793 | 0.22069051 | -1.72005490 |

| | | | |
|---|---|---|---|
| H | 0.04880943 | 0.10206137 | -1.06444181 |

(right)

Structure: $Re(NH_3)_2^+ + NH_3$ ($^5A$)
CASPT2 Energy (Ha) = -246.05799261
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 0.51019683 | 0.38958392 | -0.26883681 |
| Re | 5.66890092 | 10.51834279 | -4.11539589 |
| N | 3.83848236 | 11.56095577 | -3.60480239 |
| H | 0.36555509 | 0.63949481 | 0.77404684 |
| H | 1.15867366 | -0.47212869 | -0.35119490 |
| H | -0.44466250 | 0.17271438 | -0.72825416 |
| H | 3.88707323 | 12.60216781 | -3.82195641 |
| H | 2.98843780 | 11.16436606 | -4.10860512 |
| H | 3.62812874 | 11.47917394 | -2.53572775 |
| N | 7.49977269 | 9.47516561 | -4.63599056 |
| H | 7.43948352 | 8.43709340 | -4.41292550 |
| H | 7.72219599 | 9.55874703 | -5.67255480 |
| H | 8.33742263 | 9.85955919 | -4.10546651 |

Structure: $Re(NH_3)_3^+$ ($^5A$)
CASPT2 Energy (Ha) = -246.12313639
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 3.54858374 | 5.90579608 | -1.90861196 |
| Re | 4.27917676 | 8.00054963 | -3.26677333 |
| N | 2.45431994 | 9.06020648 | -3.78708360 |
| H | 4.32016935 | 5.25016883 | -1.57518866 |
| H | 2.88081213 | 5.33570401 | -2.51318682 |
| H | 3.01417000 | 6.23856275 | -1.04824180 |
| H | 2.46879328 | 10.04464141 | -3.38494018 |
| H | 2.35544255 | 9.13404535 | -4.84341015 |
| H | 1.54153721 | 8.58956606 | -3.42221931 |
| N | 6.27794699 | 7.16786337 | -2.90047228 |
| H | 6.38003543 | 6.19953970 | -3.32352473 |
| H | 7.03053426 | 7.77666894 | -3.33203644 |
| H | 6.48813933 | 7.10192341 | -1.86197469 |

Structure: TS ($^5A$)
CASPT2 Energy (Ha) = -246.06321611
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| N | 3.46230577 | 6.37150360 | -1.72113970 |

| | | | |
|---|---|---|---|
| Re | 4.34035835 | 7.85896978 | -3.18049796 |
| N | 2.46092698 | 8.76753203 | -3.81978777 |
| H | 3.65984303 | 6.18623974 | -3.27907501 |
| H | 2.42602718 | 6.15140972 | -1.63564342 |
| H | 3.98828812 | 5.53645276 | -1.32513097 |
| H | 2.40791884 | 9.81131117 | -3.62358420 |
| H | 2.29807013 | 8.62977908 | -4.86174448 |
| H | 1.60607365 | 8.31451359 | -3.31632909 |
| N | 6.35388391 | 7.16759070 | -2.64969551 |
| H | 6.57159872 | 6.23363231 | -3.10669363 |
| H | 7.11489764 | 7.84408823 | -2.94767939 |
| H | 6.44946864 | 7.03221328 | -1.60066286 |

Structure: H-Re$(NH_3)_2(NH_2)^+$ ($^5$A)
CASPT2 Energy (Ha) = -246.14922591
Imaginary Frequencies = 1

| | x | y | z |
|---|---|---|---|
| N | 3.45973983 | 6.75987472 | -1.49699985 |
| Re | 4.25590255 | 7.54330002 | -3.20719452 |
| N | 2.31788481 | 8.33849184 | -3.76945802 |
| H | 4.94764868 | 8.22871532 | -4.69820689 |
| H | 2.45992071 | 6.81893885 | -1.18349052 |
| H | 3.97744312 | 6.22524990 | -0.75698400 |
| H | 2.00657753 | 9.14390426 | -3.14675106 |
| H | 2.30336213 | 8.68435440 | -4.77437352 |
| H | 1.53769392 | 7.57982872 | -3.68536021 |
| N | 6.20724543 | 6.75873365 | -2.65818884 |
| H | 6.19400759 | 5.70188498 | -2.54614182 |
| H | 6.93990362 | 6.98866478 | -3.39100338 |
| H | 6.55233112 | 7.15329466 | -1.73351135 |

**Table 3**

Structure: Re$(NH_3)^+$ ($^7$A)
CASPT2 Energy (Ha) = -133.63970639
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Re | 2.04290743 | 3.50687902 | -1.38816948 |
| N | 0.91370057 | 1.46455493 | -0.60191771 |
| H | 0.63295479 | 1.50567753 | 0.45989060 |
| H | 1.53950622 | 0.56379819 | -0.67311353 |
| H | 0.01176397 | 1.23405630 | -1.13202087 |

Structure: $Re(NH_3)^+$ ($^5A$)
CASPT2 Energy (Ha) = -133.60610953
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| Re | 1.94691891 | 3.28375602 | -1.25789471 |
| N | 0.97514155 | 1.52362580 | -0.60170215 |
| H | 0.66364007 | 1.58141427 | 0.44588588 |
| H | 1.58304978 | 0.65003514 | -0.68941474 |
| H | 0.05208269 | 1.31613475 | -1.15220526 |

Structure: $Re(NH_3)_2^+$ ($^7A$)
CASPT2 Energy (Ha) = -189.87433348
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 2.46114039 | 4.76518892 | -0.78059577 |
| Re | 3.65599960 | 6.89803052 | -1.18937663 |
| H | 2.16652505 | 4.74154967 | 0.24418170 |
| H | 3.12840259 | 3.94577792 | -0.92837974 |
| H | 1.58915058 | 4.57548306 | -1.36516633 |
| N | 2.32068866 | 7.32964220 | -3.22691997 |
| H | 1.68829136 | 8.21837288 | -3.10368150 |
| H | 2.98493295 | 7.59789686 | -4.05811385 |
| H | 1.67981781 | 6.55815095 | -3.59844893 |

Structure: $Re(NH_3)_2^+$ ($^5A$)
CASPT2 Energy (Ha) = -189.91606727
Imaginary Frequencies = 0

| | x | y | z |
|---|---|---|---|
| N | 1.19936936 | 4.32408968 | -2.37760410 |
| Re | 2.41161721 | 6.07565908 | -1.98635164 |
| H | 0.26690495 | 4.58061316 | -2.81988703 |
| H | 0.98397833 | 3.78396582 | -1.48715163 |
| H | 1.68387288 | 3.64935619 | -3.04171193 |
| N | 3.62789484 | 7.81906021 | -1.59269184 |
| H | 3.86218274 | 7.94718871 | -0.56180317 |
| H | 4.58258553 | 7.80088054 | -2.12261843 |
| H | 3.15654316 | 8.74927961 | -1.91668126 |