Supporting Information

Theoretical survey of the gas-phase reactions of allylamine with Co^+

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For J. Chem. Phys. A

Fig. S1 Quintet potential energy surfaces for the most important reaction mechanisms associated with the loss of NH_3, NH_2, C_2H_2, and H_2. Numbers refer to the relative stability (in kcal/mol) with respect to the **AA** + Co^+ entrance channel evaluated at the B3LYP/6-311+G(2df,2pd)//6-311++G(d,p) level and including ZPE corrections. (a) Direct β-H-migration mechanism for the loss of NH_3 and NH_2. (b) Cyclization–hydrogen migration mechanism for the loss of NH_3 and NH_2. (c) Loss of C_2H_2. (d) 2,3-H_2 elimination.

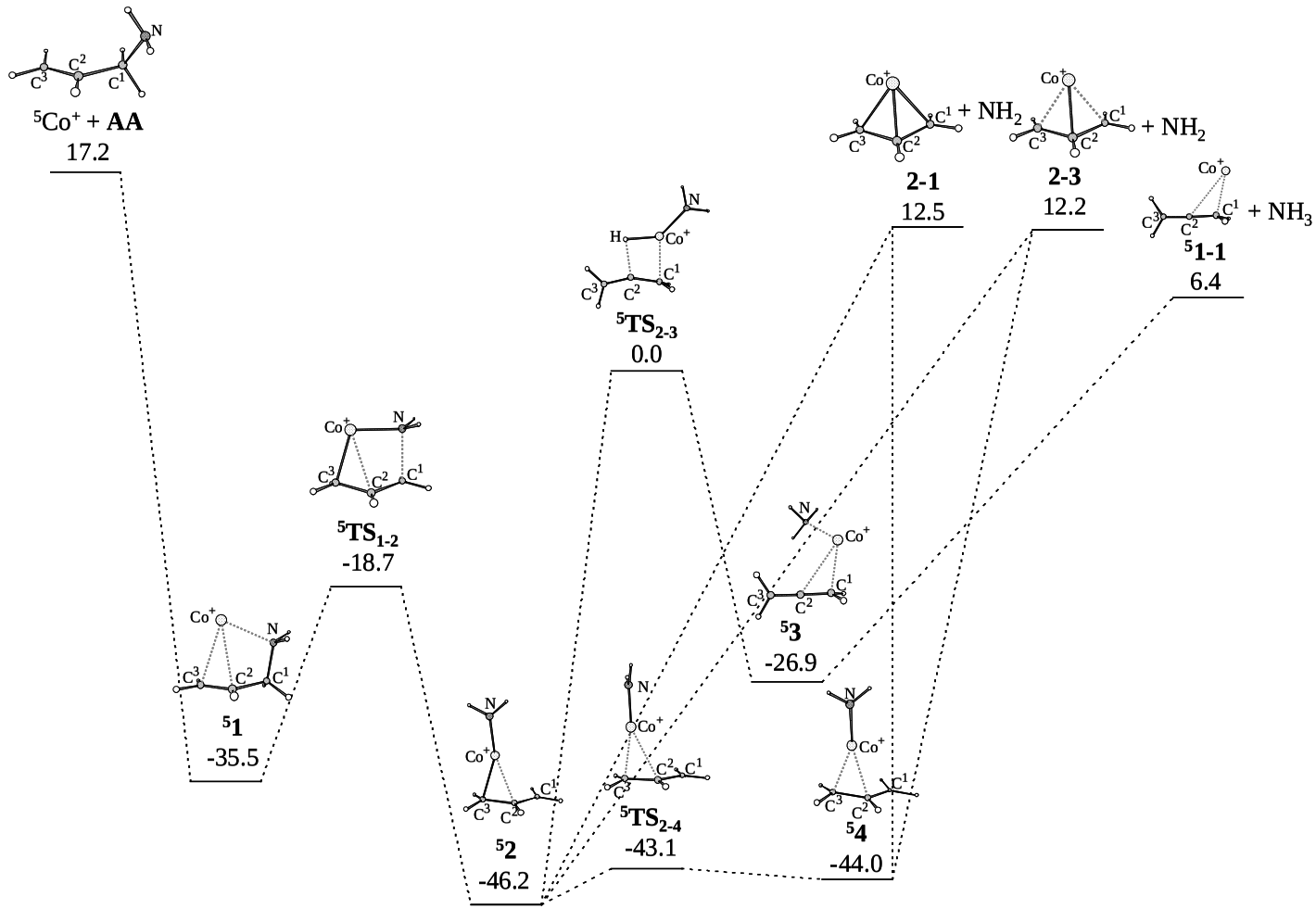

5Co+ + AA
17.2
5TS1-2
-18.7
51
-35.5
52
-46.2
5TS2-3
0.0
5TS2-4
-43.1
53
-26.9
54
-44.0
2-1
12.5
2-3
12.2
51-1
6.4
+ NH2
+ NH2
+ NH3

Figure S1 (a)

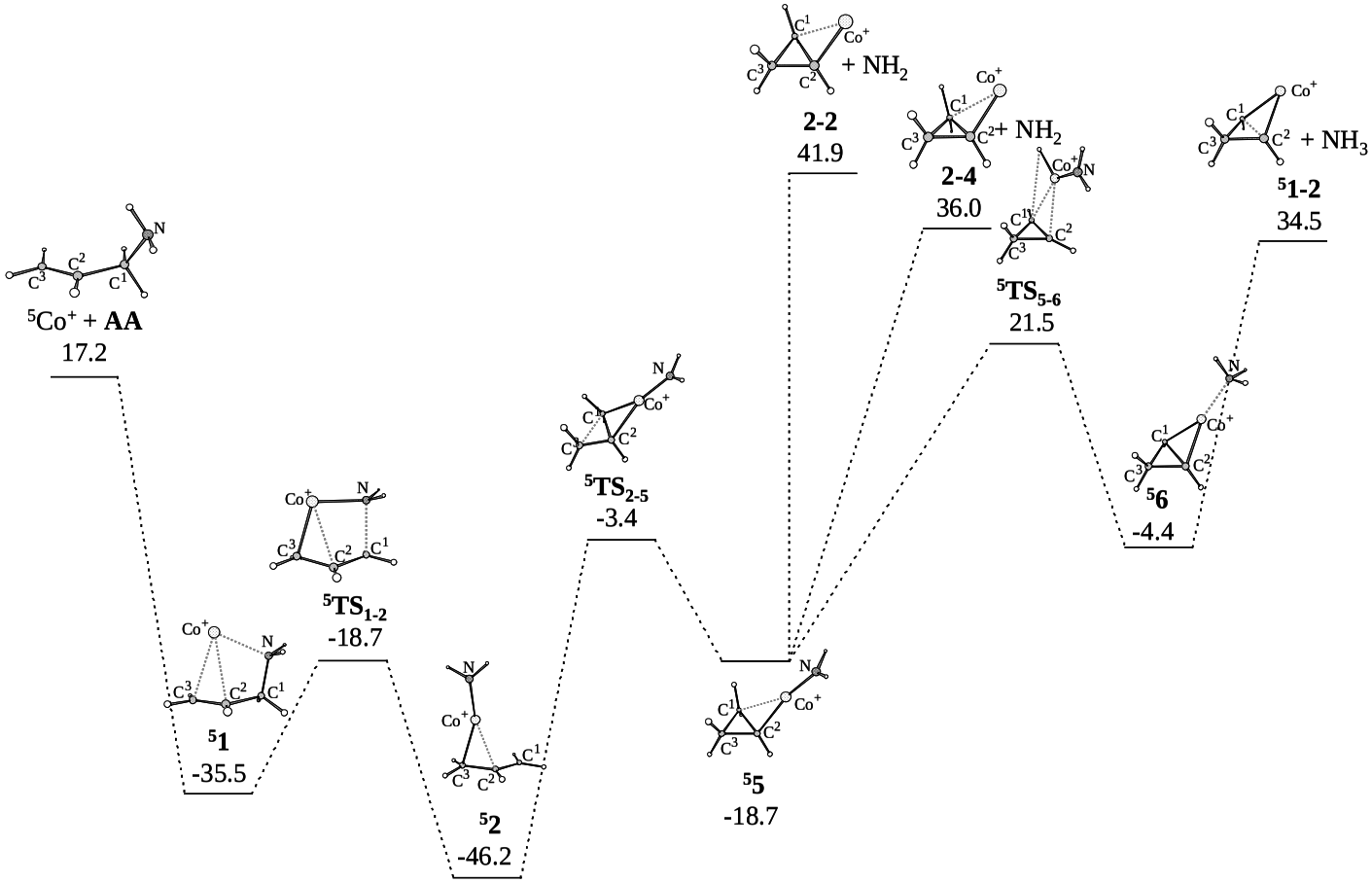

^{5}Co$^+$ + **AA**
17.2
^{5}**1**
-35.5
^{5}**TS$_{1-2}$**
-18.7
^{5}**2**
-46.2
^{5}**TS$_{2-5}$**
-3.4
^{5}**5**
-18.7
2-2
41.9
+ NH$_2$
2-4
36.0
+ NH$_2$
^{5}**TS$_{5-6}$**
21.5
^{5}**6**
-4.4
^{5}**1-2**
34.5
+ NH$_3$

Figure S1 (b)

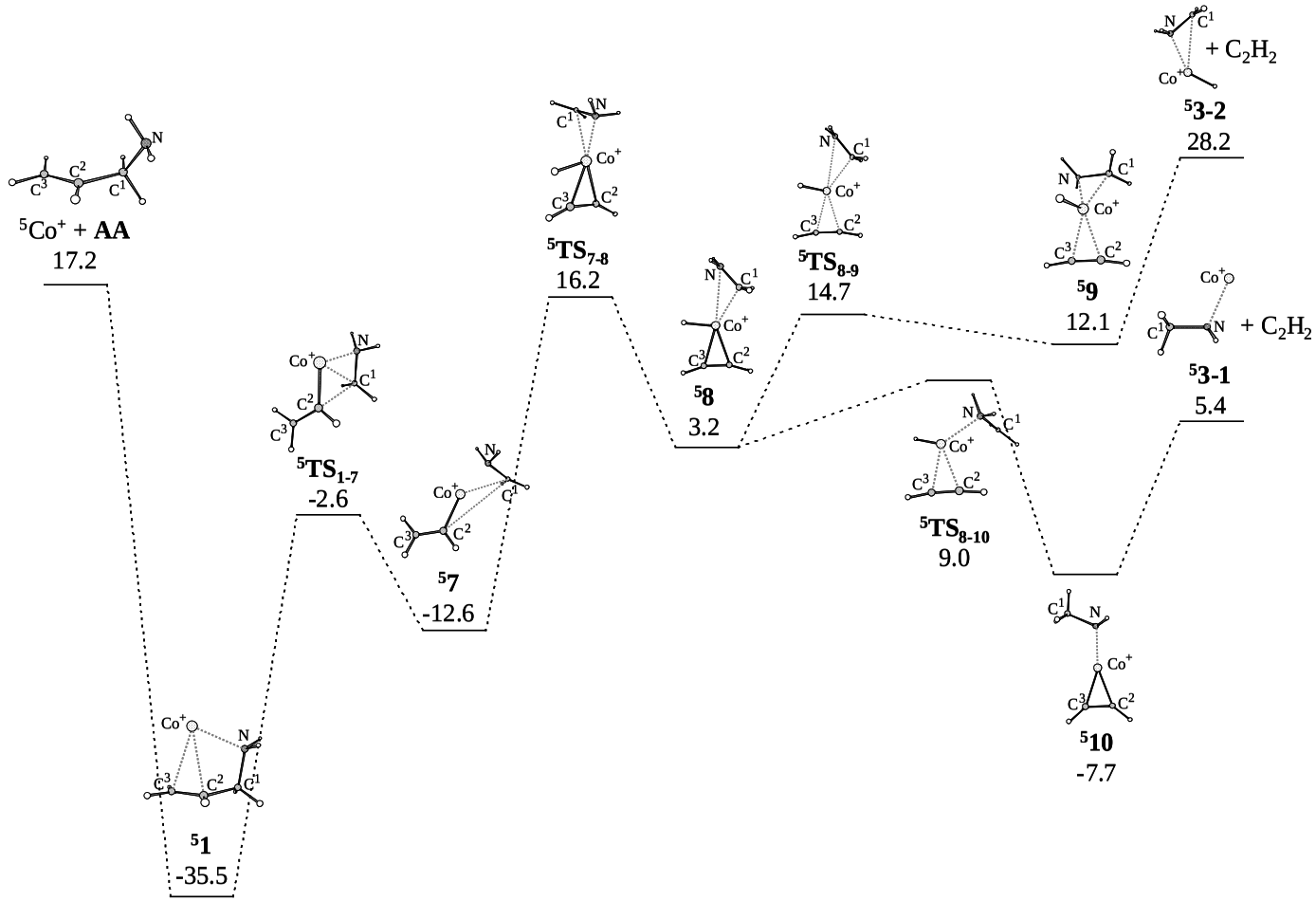

^{5}Co$^+$ + **AA**
17.2
^{5}**1**
-35.5
^{5}**TS$_{1-7}$**
-2.6
^{5}**7**
-12.6
^{5}**TS$_{7-8}$**
16.2
^{5}**8**
3.2
^{5}**TS$_{8-9}$**
14.7
^{5}**9**
12.1
^{5}**TS$_{8-10}$**
9.0
^{5}**10**
-7.7
^{5}**3-2**
28.2
+ C_2H_2
^{5}**3-1**
5.4
+ C_2H_2

Figure S1 (c)

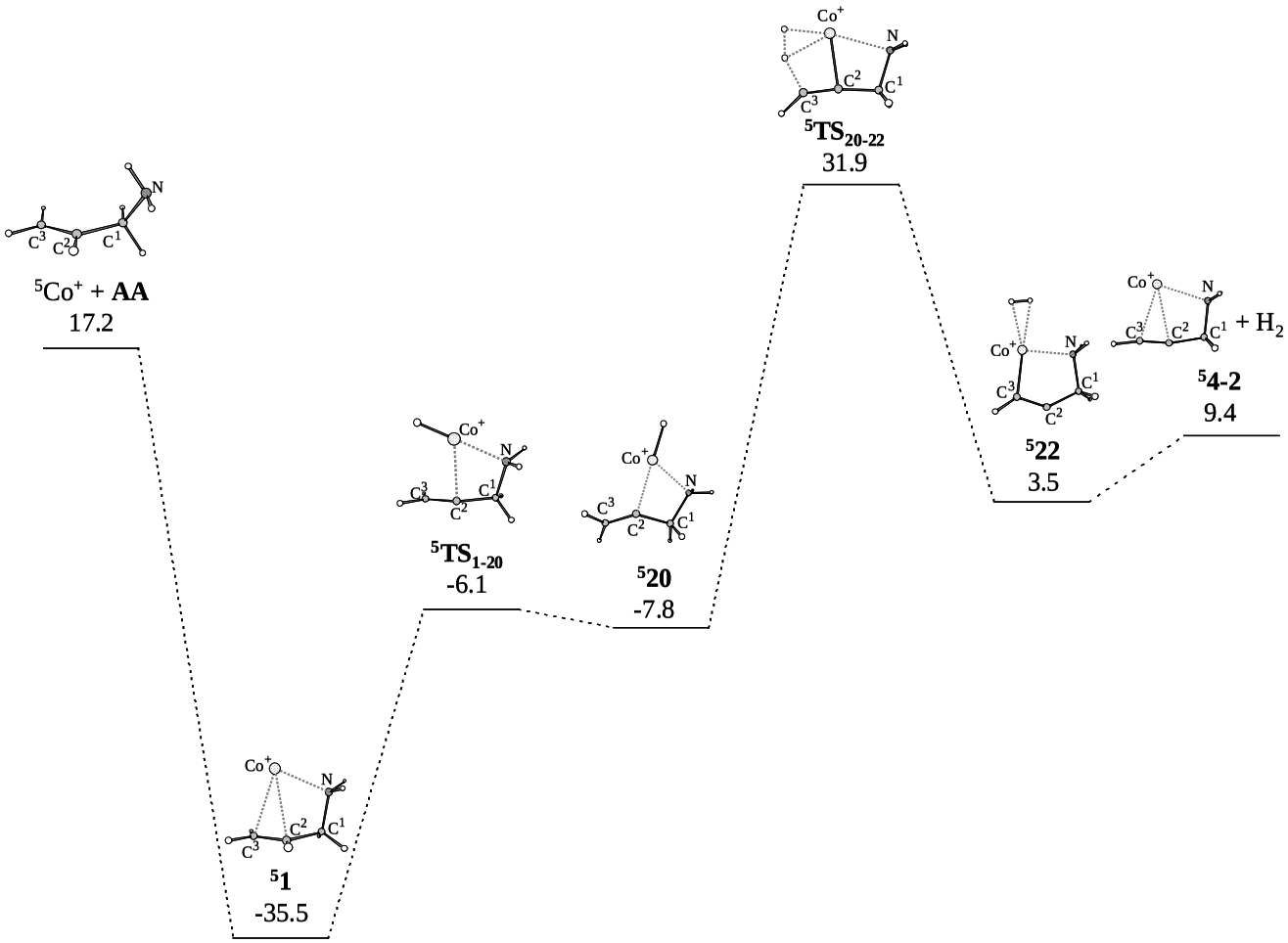
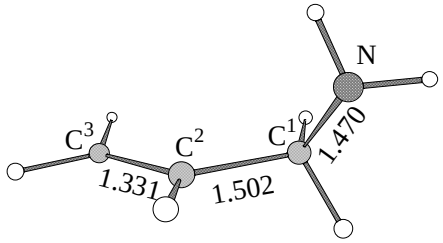

^{5}Co$^+$ + **AA**
17.2
^{5}**1**
-35.5
^{5}**TS$_{1\text{-}20}$**
-6.1
^{5}**20**
-7.8
^{5}**TS$_{20\text{-}22}$**
31.9
^{5}**22**
3.5
^{5}**4-2**
9.4
+ H$_2$

Figure S1 (d)

Fig. S2 Optimized structures (in Cartesian coordinate) and relative stabilizations (kcal/mol) with respect to **AA** for the conformational isomers of allylamine.

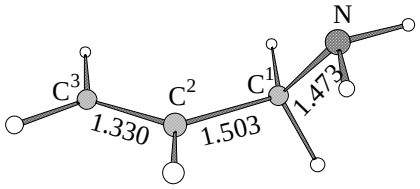
AA1



0.04 kcal/mol

C	1.84064400	0.01922000	-0.25833200
C	0.69624800	-0.28523100	0.34944900
H	2.72935700	-0.58996600	-0.13758200
H	1.93074200	0.89464300	-0.89525800
H	0.62785300	-1.17536400	0.97095900
C	-0.57030900	0.51511700	0.23703100
H	-0.83466400	0.90217700	1.22845800
H	-0.39343000	1.38709300	-0.41112500
N	-1.68021800	-0.34359800	-0.19995100
H	-2.56296900	0.15509200	-0.17247600
H	-1.53486100	-0.66312200	-1.15220200

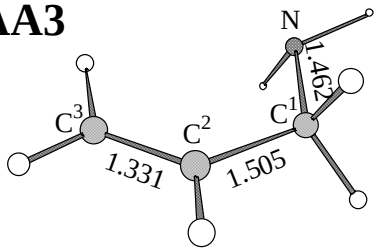
AA2



1.50 kcal/mol

C	1.86053700	0.07009600	-0.23056300
C	0.69361300	-0.36206300	0.23821300
H	2.73893800	-0.56528900	-0.24398900
H	1.97937800	1.07714900	-0.61902900
H	0.61718700	-1.38214600	0.61424000
C	-0.56263300	0.45800500	0.32146200
H	-0.78480700	0.64665000	1.38595500
H	-0.39368700	1.43160100	-0.14707300
N	-1.67381300	-0.20420200	-0.38413700
H	-2.52574000	0.34095400	-0.29766300
H	-1.86367200	-1.11573200	0.02184700

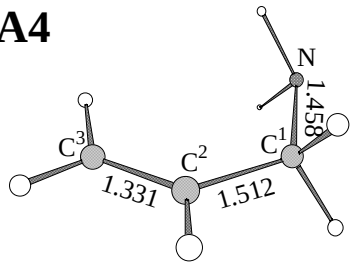
AA3



0.48 kcal/mol

C	-1.52710300	-0.55767200	-0.04036800
C	-0.81825500	0.56570200	0.03901000
H	-2.60928500	-0.54180200	0.02017100
H	-1.04852600	-1.51922100	-0.18528200
H	-1.33307100	1.51589500	0.16884600
C	0.68179800	0.67063400	-0.02530500
H	1.01057500	1.32204500	0.80295600
H	0.95314300	1.20423200	-0.94522600
N	1.34863400	-0.63028900	-0.04786500
H	2.34487100	-0.52412400	-0.20062100
H	1.22321700	-1.11698600	0.83418400

AA4



0.08 kcal/mol

C	-1.52885300	-0.55326800	0.00006300
C	-0.81398300	0.56907500	0.00001800
H	-2.61235800	-0.53263500	0.00006900
H	-1.06120200	-1.53266000	0.00010600
H	-1.33381300	1.52674500	-0.00005100
C	0.69444200	0.67388000	-0.00002200
H	0.99949700	1.26916600	0.86976300
H	0.99936800	1.26939400	-0.86971300
N	1.47741200	-0.55642400	-0.00019100
H	1.27957700	-1.12109000	0.81921100
H	1.27741100	-1.12207200	-0.81840800

Figure S2

Fig. S3 Optimized geometries and selected structural parameters (in angstrom and deg) for all the intermediates, saddle points and products for the loss of NH_3 and NH_2 at the B3LYP/6-311++G(d,p) level of theory. (a) Direct β-H-migration mechanism (b) Cyclization–hydrogen migration mechanism.

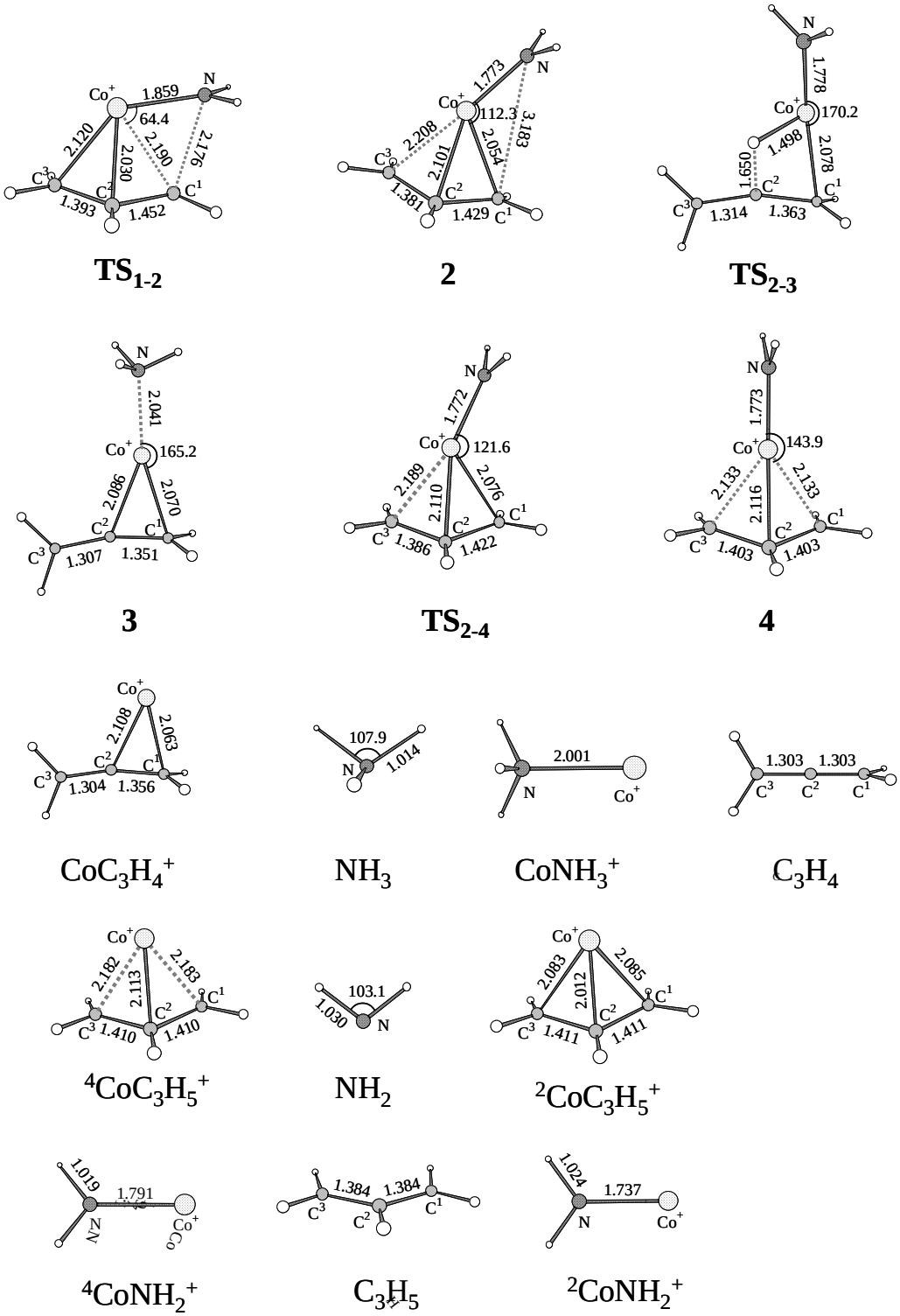
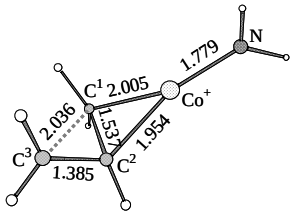
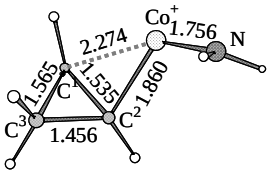

TS1-2
2
TS2-3
3
TS2-4
4
CoC3H4+
NH3
CoNH3+
C3H4
4CoC3H5+
NH2
2CoC3H5+
4CoNH2+
C3H5
2CoNH2+

Figure S3 (a)



$TS_{2\text{-}5}$



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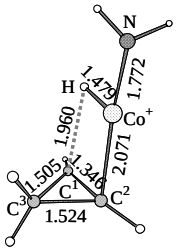
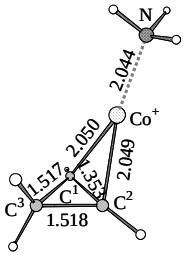


$TS_{5\text{-}6}$



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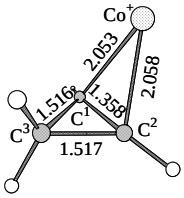
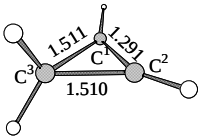
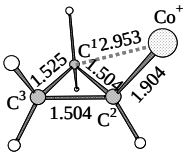


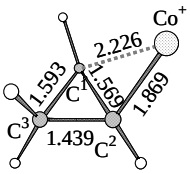
c-$CoC_3H_4^+$



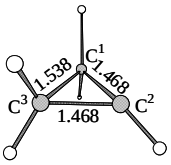
c-C_3H_4



c-$^4CoC_3H_5^+$



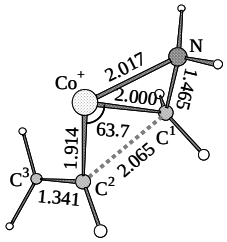
c-$^2CoC_3H_5^+$



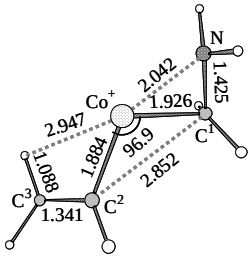
c-C_3H_5

Figure S3 (b)

Fig. S4 Optimized geometries and selected structural parameters (angstrom and deg) for all the intermediates, saddle points and products involved in the loss of C_2H_2 at the B3LYP/6-311++G(d,p) level of theory.



$TS_{1\text{-}7}$



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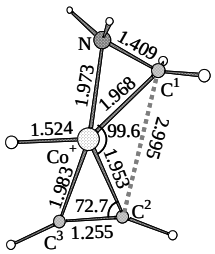
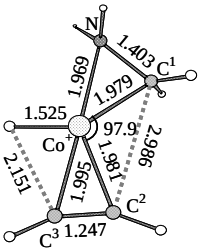


$TS_{7\text{-}8}$



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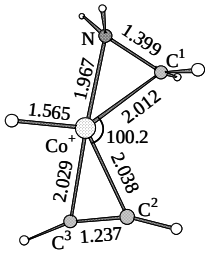
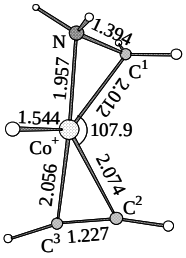


$TS_{8\text{-}9}$



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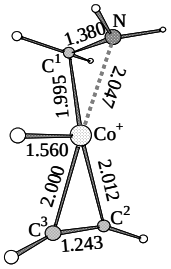
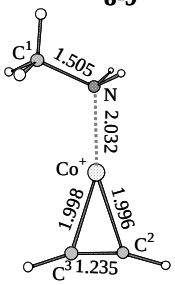


$TS_{8\text{-}10}$



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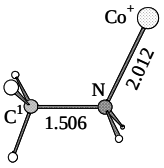
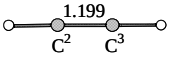
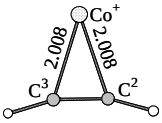


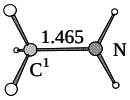
$Co^{+}NH_2CH_3$



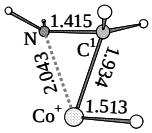
C_2H_2



$CoC_2H_2^{+}$



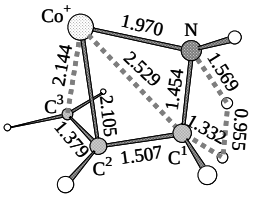
CH_3NH_2



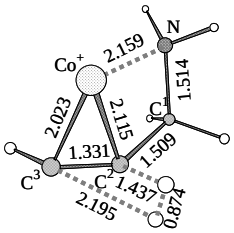
$HCo^{+}(NH_2CH_2)$

Figure S4

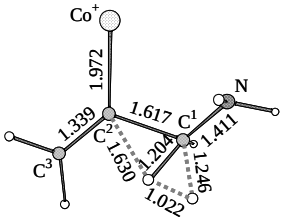
Fig. S5 Optimized geometries and selected structural parameters (angstrom and deg) for all the intermediates, saddle points and products involved in “direct” mechanisms for the loss of H_2 at the B3LYP/6-311++G(d,p) level of theory.



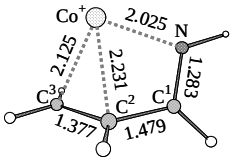
$TS_{1\text{-}D1}$



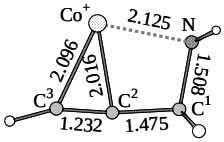
$TS_{1\text{-}D2}$



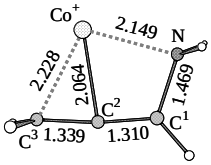
$TS_{1\text{-}D3}$



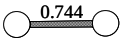
$Co^+(NHCHCHCH_2)$



$Co^+(NH_2CH_2CCH)$



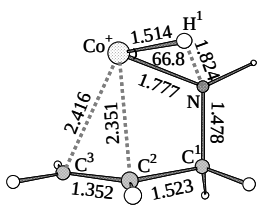
$Co^+(NH_2CHCCH_2)$



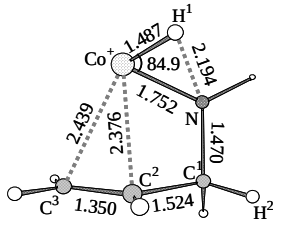
H_2

Figure S5

Fig. S6 Optimized geometries and selected structural parameters (angstrom and deg) for all the intermediates and saddle points involved in the initial N-H activation mechanism for the loss of H_2 at the B3LYP/6-311++G(d,p) level of theory.



$TS_{1\text{-}11}$



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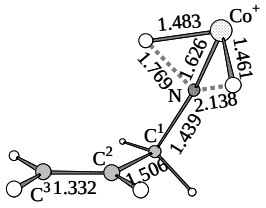

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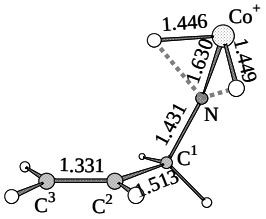

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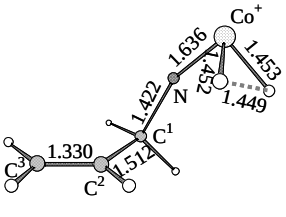

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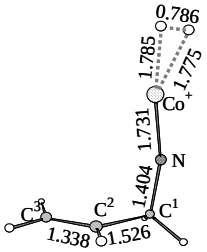

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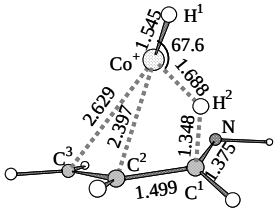

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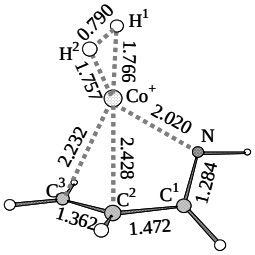

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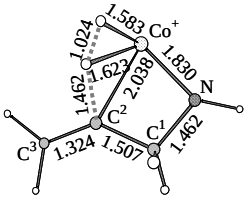

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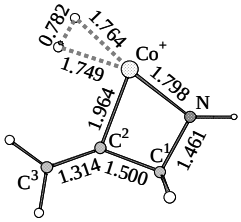

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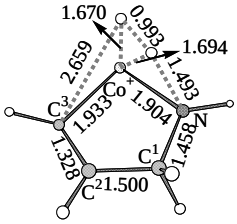

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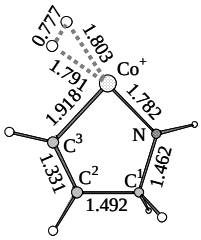

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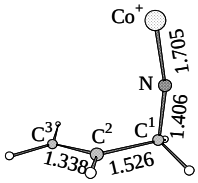
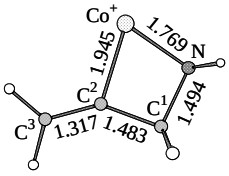
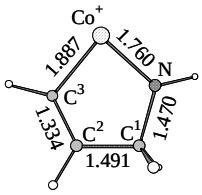


$Co^+(NCH_2CHCH_2)$



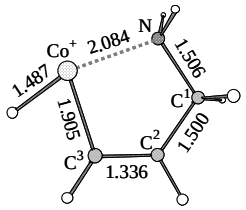
$Co^+(NHCH_2CCH_2)$



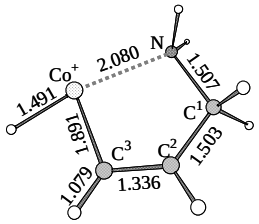
$Co^+(NHCH_2CHCH)$

Figure S6

Fig. S7 Optimized geometries and selected structural parameters (angstrom and deg) for all the intermediates, saddle points and products in the initial C-H activation mechanisms for the loss of H_2 at the B3LYP/6-311++G(d,p) level of theory.



$TS_{1\text{-}17}$



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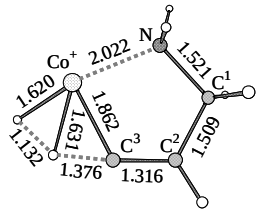
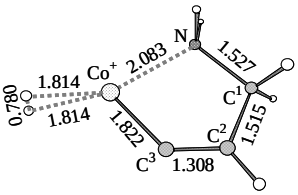


$TS_{17\text{-}18}$



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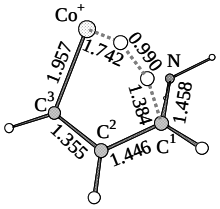

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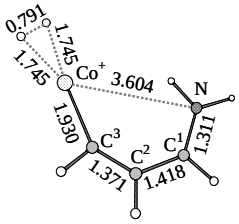

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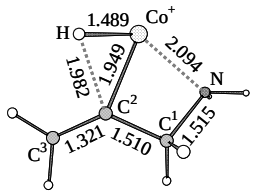

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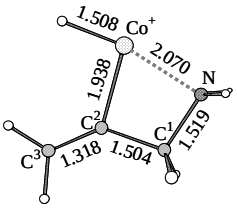

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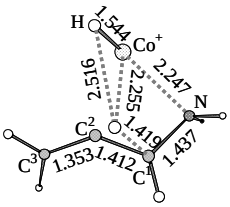

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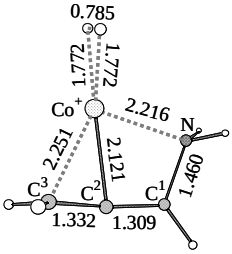

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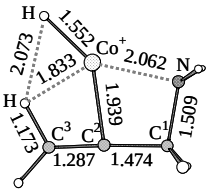

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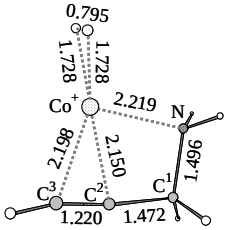

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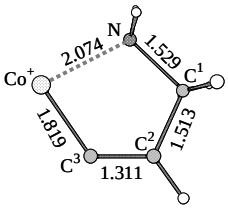
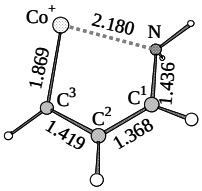


$Co^{+}(NH_2CH_2CHC)$



$Co^{+}(NH_2CHCHCH)$

Figure S7

Table S1. Total energies E (in hartree), zero-point energies ZPE (in kcal/mol) and $<S^2>$ for all the species involved in the reactions of allylamine with Co^+.

Species	B3LYP/6-311++G(d,p)[a]			B3LYP/6-311+G(2df,2pd)[a]	
	E	ZPE	$<S^2>$[b]	E	$<S^2>$[b]
Co^+	-1382.4197362	0	2.00	-1382.4202676	2.00/2.00
AA	-173.3097539	58.71	0.00	-173.3219052	0.00
AA1	-173.3098208	58.76	0.00	-173.3219211	0.00
AA2	-173.3069576	58.56	0.00	-173.3192894	0.00
AA3	-173.308993	58.75	0.00	-173.3212089	0.00
AA4	-173.3097595	58.80	0.00	-173.3219404	0.00
1	-1555.8449959	60.52	2.02	-1555.8562259	2.02
TS_{1-2}	-1555.7995764	58.24	2.09	-1555.8072915	2.05
2	-1555.8204281	57.54	2.16	-1555.8335429	2.16
TS_{2-3}	-1555.7510076	53.23	2.07	-1555.764643	2.07
3	-1555.8531051	57.56	2.02	-1555.8538202	2.01
TS_{2-4}	-1555.820244	59.75	2.16	-1555.8313741	2.14
4	-1555.8211107	59.92	2.15	-1555.8342052	2.15
$CoC_3H_4^+$	-1499.1897915	35.36	2.01	-1499.1857185	2.01
NH_3	-56.5827213	21.50	0.00	-56.5872248	0.00
$^4CoC_3H_5^+$	-1499.799647	42.62	3.76	-1499.8079521	3.76
NH_2	-55.900417	11.86	0.75	-55.9045773	0.75
$^2CoC_3H_5^+$	-1499.8112899	43.42	1.10	-1499.8087794	0.85
TS_{2-5}	-1555.7619535	56.79	2.08	-1555.7741502	2.04
5	-1555.7694341 -1555.775234	59.77 59.64	2.12 2.09	-1555.7839072 -1555.7885971	2.14 2.08
TS_{5-6}	-1555.7141524	53.51	2.06	-1555.7248375	2.04
6	-1555.8133806	58.15	2.03	-1555.8142635	2.03
c-$CoC_3H_4^+$	-1499.1488379	34.50	2.02	-1499.1532742	2.02
c-$^4CoC_3H_5^+$	-1499.7662971	41.61	3.76	-1499.7710265	3.76
c-$^2CoC_3H_5^+$	-1499.7503301 -1499.7528149	42.89 43.38	1.26 1.23	-1499.7592665 -1499.761803	1.21 1.19

TS_{1-7}	-1555.7843423	60.74	2.03	-1555.7958707	2.02
7	-1555.7935573	60.44	2.04	-1555.8050613	2.03
TS_{7-8}	-1555.7526963	56.93	2.03	-1555.7645138	2.02
8	-1555.7528461	57.26	2.03	-1555.7641006	2.02
TS_{8-9}	-1555.7475861	56.19	2.05	-1555.7506946	2.02
9	-1555.7489207	56.84	2.03	-1555.7605764	2.02
TS_{8-10}	-1555.735695	55.92	2.19	-1555.7464136	2.05
10	-1555.833469	60.01	2.02	1555.84296	2.02
$Co^{+}NH_2CH_3$	-1478.4060105	42.25	2.02	-1478.4132765	2.05
C_2H_2	-77.3566623	15.88	0.00	-77.3620078	0.00
$Co^{+}H(NH_2CH_2)$	-1478.3616588	38.56	2.03	-1478.3690585	2.02
TS_{1-D1}	-1555.6940666	54.54	2.05	-1555.7062409	2.04
TS_{1-D2}	-1555.6624106	53.80	2.03	-1555.6699311	2.03
TS_{1-D3}	-1555.6732541	54.82	2.02	-1555.6813592	2.03
$Co^{+}(NHCHCHCH_2)$	-1554.6180966	47.55	2.03	-1554.6267921	2.02
$Co^{+}(NH_2CH_2CCH)$	-1554.590049	45.90	2.02	-1554.6021022	2.01
$Co^{+}(NH_2CHCCH_2)$	-1554.5896027	45.65	2.01	-1554.5993359	2.02
H_2	-1.1795715	6.32	0.00	-1.1800116	0.00
TS_{1-11}	-1555.7597355	58.27	2.05	-1555.7712965	2.02
11	-1555.7612197	58.53	2.05	-1555.7737317	2.03
TS_{11-12}	-1555.6633991	51.80	2.08	-1555.6765062	2.05
12	-1555.6649095	52.52	2.09	-1555.6769796	2.07
TS_{12-13}	-1555.6635492	51.58	2.08	-1555.6763228	2.05
13	-1555.7157951	53.10	2.71	-1555.7284475	2.68
TS_{11-14}	-1555.7102148	54.62	2.65	-1555.7148034	2.16
14	-1555.8167769	56.82	2.02	-1555.8273517	2.02
TS_{11-15}	-1555.6988344	52.17	2.18	-1555.708646	2.07
15	-1555.7316334	53.45	2.18	-1555.744716	2.15
TS_{11-16}	-1555.7021721	52.58	2.30	-1555.7144732	2.24

16	-1555.7482925	54.14	2.12	-1555.7596912	2.06
$Co^{+}(NCH_2CHCH_2)$	-1554.5090806	43.93	2.64	-1554.516429	2.51
$Co^{+}(NHCH_2CCH_2)$	-1554.5285873	44.19	2.12	-1554.5377706	2.14
$Co^{+}(NHCH_2CHCH)$	-1554.5463512	44.63	2.12	-1554.5563798	2.06
$TS_{1\text{-}17}$	-1555.7887344	56.96	2.05	-1555.7996421	2.06
17	-1555.7893878	57.54	2.06	-1555.801923	2.06
$TS_{17\text{-}18}$	-1555.700895	54.42	2.06	-1555.71229	2.05
18	-1555.7513366	54.87	2.04	-1555.7634187	2.03
$TS_{17\text{-}19}$	-1555.7159197	53.42	2.43	-1555.7216208	2.20
19	-1555.7886765	55.38	2.02	-1555.7904581	2.01
$TS_{1\text{-}20}$	-1555.7716797	56.55	2.06	-1555.786266	2.03
20	-1555.7727337	56.76	2.10	-1555.7737998	2.11
$TS_{20\text{-}21}$	-1555.6827345	52.21	2.58	-1555.685011	2.07
21	-1555.7896328	54.52	2.01	-1555.8005715	2.01
$TS_{20\text{-}22}$	-1555.734859	54.96	2.18	-1555.748423	2.12
22	-1555.7859965	54.85	2.01	-1555.8030603	2.01
$Co^{+}(NH_2CH_2CHC)$	-1554.5485428	45.98	2.11	-1554.5547875	2.03
$Co^{+}(NH_2CHCHCH)$	-1554.5756548	45.78	2.34	-1554.5837548	2.16

[a] The upper/lower values are values without/with wavefunction optimization when there are two rows for a species. [b] Values before annihilation.