Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

For

Mechanistic Insights into Hydride Transfer for Catalytic Hydrogenation of CO_2 with Cobalt Complexes

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Computational Details: All calculations in the present study were performed using *Gaussian* 09 suite of programs.[1] To characterize all the reaction intermediates and transitions states involved in these two pathways (*direct hydride transfer* and *associative* pathway), we applied quantum mechanical calculations based on density function theory (DFT). The hybrid B3P86[2] functional was used with the Stuttgart-Dresden relativistic effective core potential for Co and its associated basis set (SDD) [3], while the 6-31G** basis set was used for all the non-metal atoms. This level of theory (B3P86) has been shown to provide high accuracy for the prediction of the thermodynamics properties (hydricities, acidities, and reduction potentials) and reactivity of cobalt and nickel hydride complexes.[4] Harmonic vibrational frequencies were calculated at the optimized geometries using the same level of theory to estimate the zero-point energy (ZPE) and the thermal contributions (298 K and 1 atm) to the free energy. The energetic stability of all the intermediates and transition states involved in the reaction pathway have been verified by additional intrinsic reaction coordinate (IRC) calculations.

The thermodynamics data were determined experimentally in acetonitrile (MeCN) solution, whereas the catalytic studies were investigated in tetrahydrofuran (THF), so the calculations were performed in either solvent. In addition, all stationary points were optimized both in the gas-phase as well in solution. The latter was described using the SMD continuum model[5] of solvation in connection with the Bondi[6] radii with no additional scaling factors. We further tested the accuracy of SMD model by incorporating additional diffuse functions one each nonmetal (6-31+G**) while keeping the same basis set for the Co metal, the relative free energy barriers of the two pathways are independent of the basis set. However, the overall free energy of the reaction found to be highly exothermic in both THF and CH_3CN solution (almost 14 kcal/mol lower than its value with 6-31G** both in THF as well as in MeCN). This is consistent

with the original SMD paper by Truhlar et al[5], in which they clearly discussed that a basis set containing diffuse functions (6-31+G**) tends to produce negative solvation energies.[5] Moreover, the calculated overall free energy for the formation of formate with a 6-31G** basis set is -6.2 kcal/mol in MeCN (-21.2 kcal/mol with 6-31+G** in CH_3CN solution) which is in good agreement with its -8.0 kcal/mol experimental value. As a result, we utilized 6-31G** basis set for all the calculations involved in both pathways.

We further confirmed the energetics of both pathways (*direct hydride transfer* and *associative*) using dispersion corrected (S6 scaling factor on Grimme's long range dispersion correction is 0.25) M06 exchange correlation functional in order to understand the role of dispersion forces and nonbonding interactions of CO_2 and $Co(dmpe)_2H$.[7] The calculated free energy profiles of *direct hydride transfer* and *associative* are shown in Figure S7 and Figure S8, respectively. The relative changes in free energy barriers for both the mechanisms are almost similar to that of B3P86 functional, yet the absolute values are different. In the present contribution, the choice of the B3P86 exchange correlation functional is based on its good agreement to the observed experimental rate as well as overall free energy of the reaction (in MeCN).

Natural Bond Orbital (NBO) Analysis: To characterize the nature of the Co···H-CO_2 interactions in the H-bound formate $Int1_D$ ($Int2_A$) complex involved in the *direct hydride transfer* and *associative* pathways, we carried out a Natural Bond Orbital (NBO) analysis[8] using the same level of theory. The NBO analysis indicates a charge transfer of 0.13e between the lone pair (nonbonding orbital) of the hydrogen-bond acceptor Co(I) and the antibonding σ*(C-H) orbital of formate (See natural orbitals in Figure S3), suggesting that $Int1_D$ complex is stabilized by a strong hydrogen bond. Because of this hydrogen bond, the hydride transfer reaction is exergonic (-6.0 kcal/mol in THF and -9.7 kcal/mol in MeCN) with respect to RC_T (Figure 3), while slightly endergonic in THF (+1.1 kcal/mol) and exergonic in MeCN (-4.7 kcal/mol) relative to the energy of CO_2 and $Co(dmpe)_2H$. In addition, the charges on each of the atom (such as Co, H and CO2) involved in all the key species in both pathways have been calculated and listed in Table S2.

Table S1. Kinetic Parameters for Both Calculated Pathways and Comparison with Experimental Data

	direct		***associative***		**exp.**[9]
	H	D	H	D	H
Free energy of activation (kcal/mol)	17.24	17.42	15.85	15.80	17.50
Rate constant (s^{-1})	1.44	1.08	14.99	16.31	0.94
KIE (K_H/K_D)	1.33 (1.32)[a]		0.92 (0.96)[a]		

[a]KIE values shown in the bracket are calculated with a large basis set (Co-(SDD) and 6-311+G(d, p) on all the atoms) to verify the nature of the distinct KIE for both pathways.

Table S2. Calculated Charges from Natural Bond Orbital (NBO) Analysis for all the Key Species Involved in *Direct Hydride Transfer* and *Associative* Pathway.

NBO charges	***Direct hydride transfer***			***Associative* pathway**			
Atoms	RC_D	$TS1_D$	$Int1_D$	RC_A	$TS1_A$	$Int1_A$	$TS2_A$
Co	-2.15	-1.88	-1.35	-2.16	-2.07	-2.00	-1.76
H	0.14	0.04	0.07	0.15	0.15	0.21	0.20
C	1.05	0.98	0.68	1.05	1.02	0.81	0.75
O	-0.52	-0.58	-0.73	-0.52	-0.55	-0.71	-0.73
O	-0.53	-0.58	-0.73	-0.52	-0.57	-0.74	-0.72

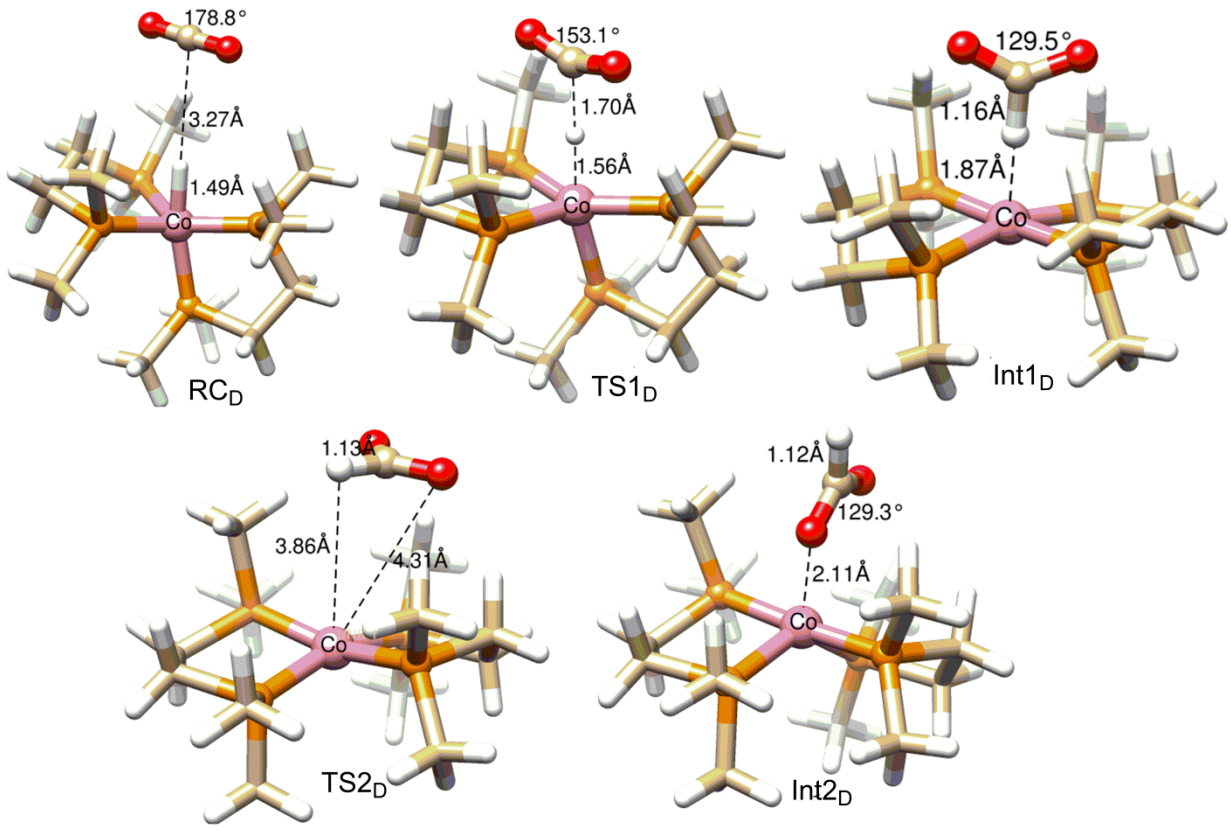

Figure S1. Optimized geometries (in THF) of all the species involved in the *direct hydride transfer* pathway.

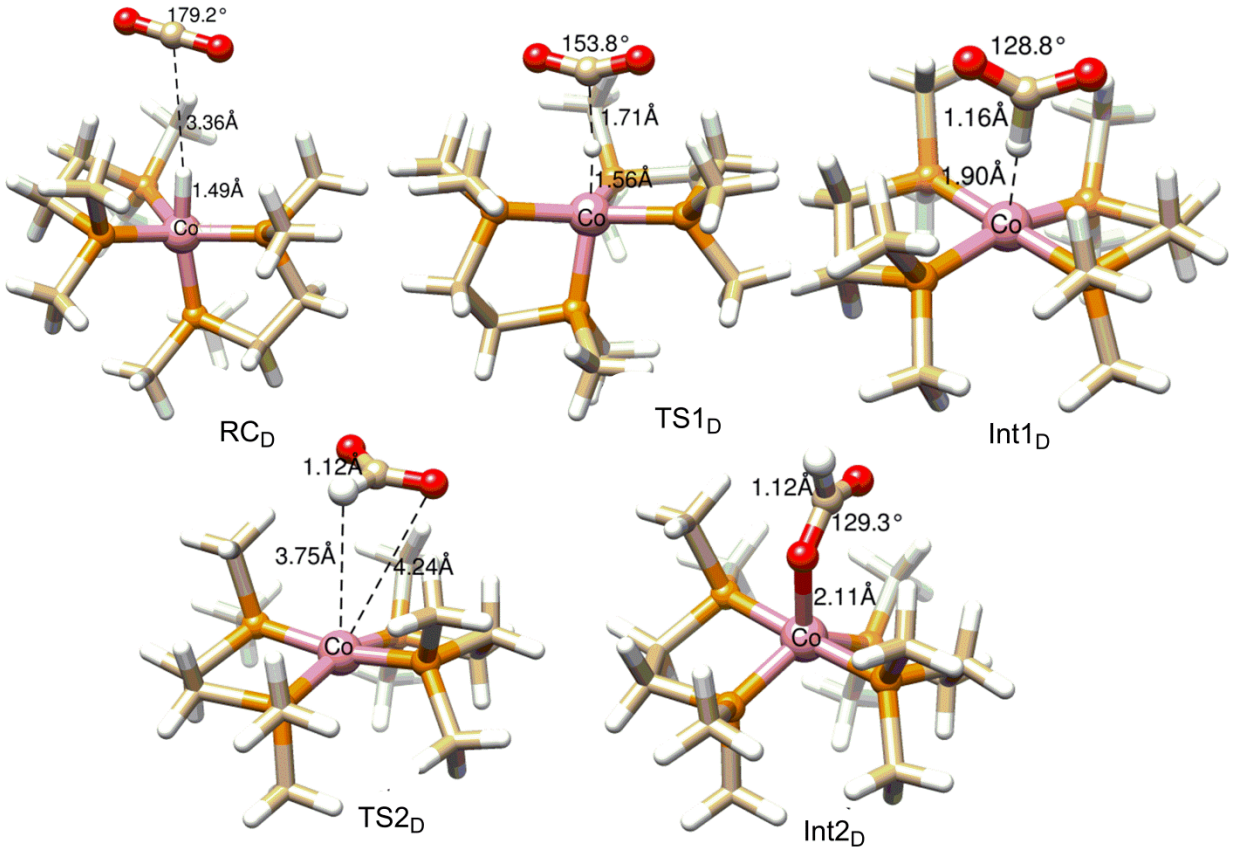

Figure S2. Optimized geometries (in CH_3CN) of all the species involved in *direct hydride transfer* pathway.

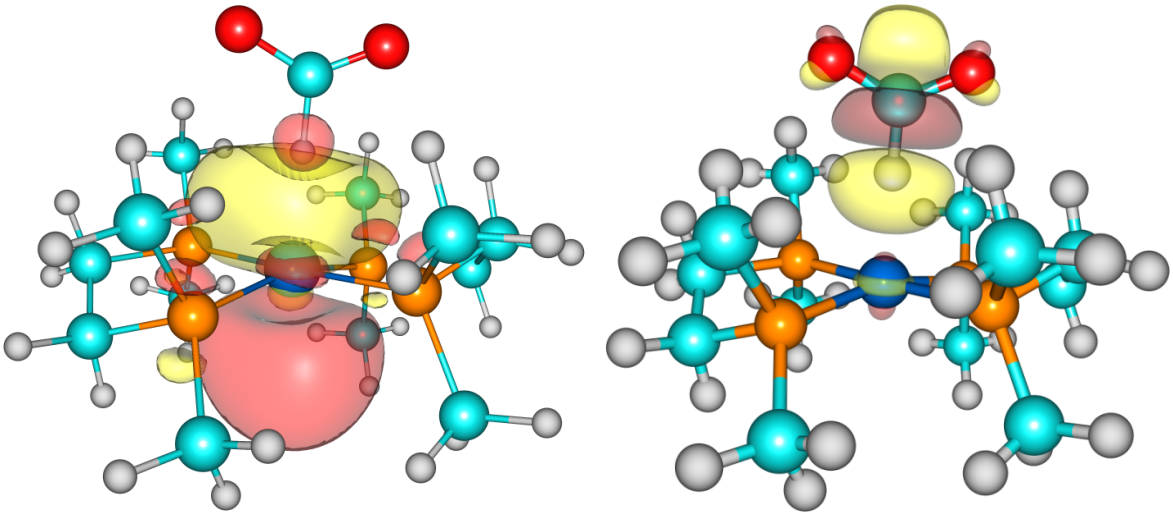

Figure S3. Natural Bonding Orbital (NBO) analysis showing charge transfer between lone pair of the hydrogen-bond acceptor Co(I) (left, orbital 98) and the antibonding σ*(C–H) orbital of formate (right, orbital 437).

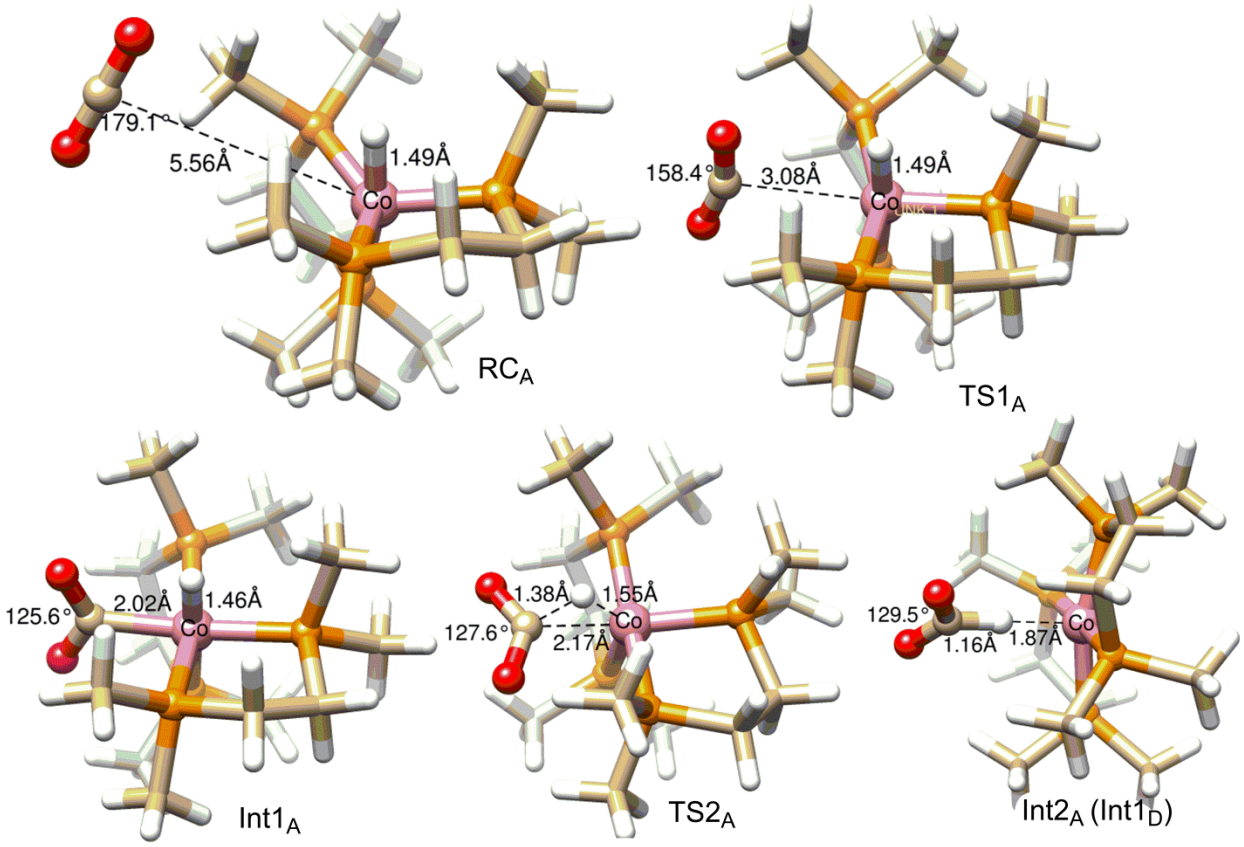

Figure S4. Optimized geometries (in THF) of all the species involved in the *associative* pathway.

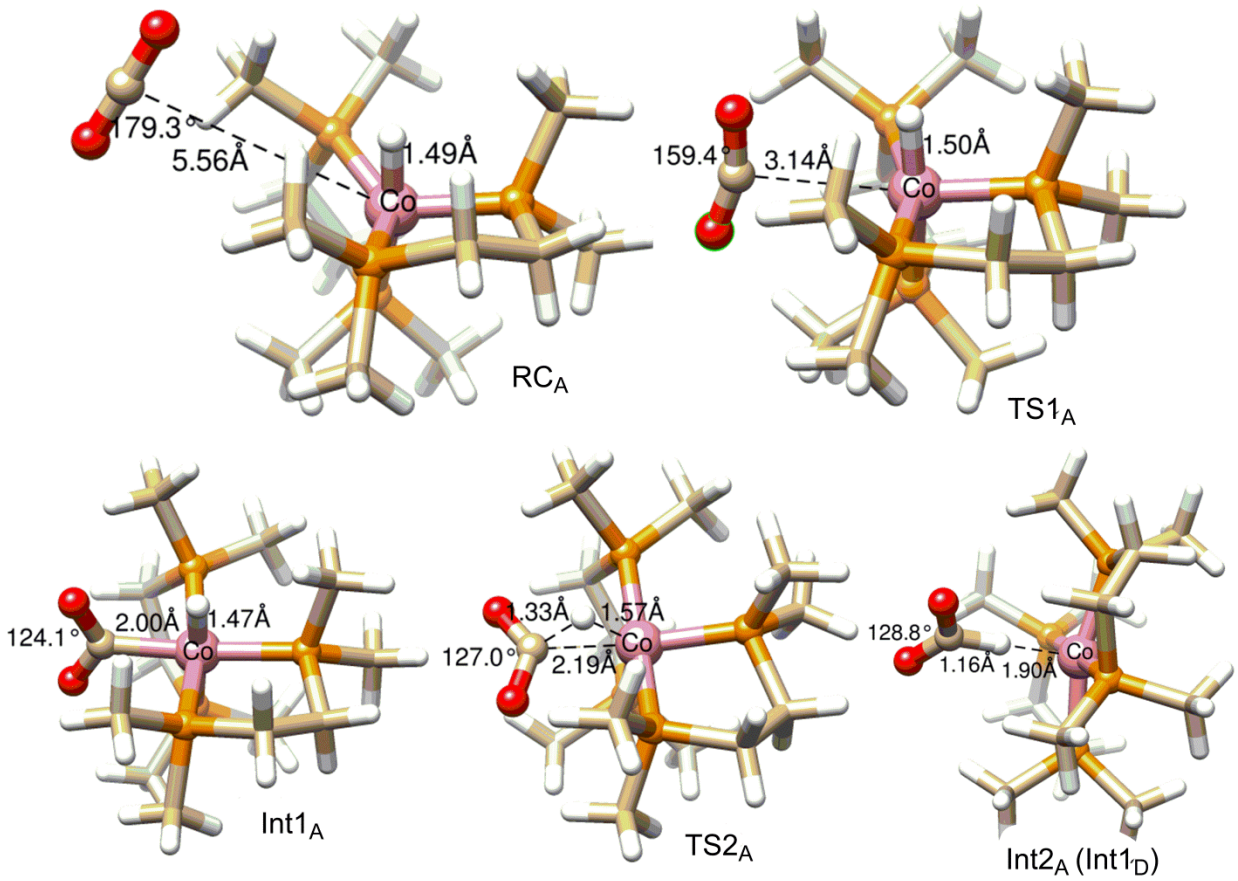

Figure S5. Optimized geometries (in CH_3CN) of all the species involved in *associative* pathway.

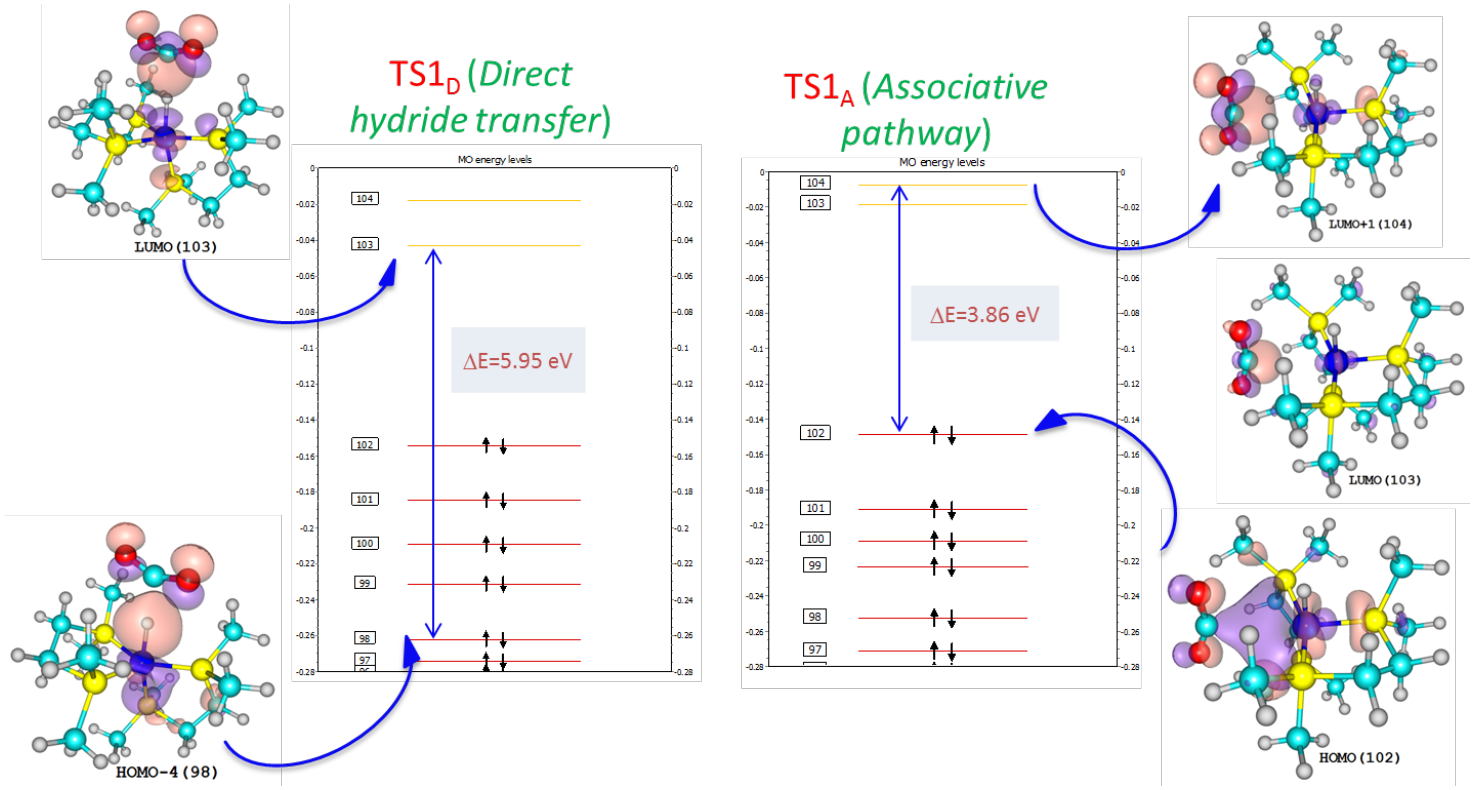

Figure S6. Molecular orbitals energy diagram (showing the energy gap) for the rate limiting transition states of both *direct* and *associative* pathways. The bonding (HOMO) and corresponding antibonding (LUMO) combinations involved in both the transition states (hydride transfer in $TS1_D$ [left] and the binding of CO2 to the cobalt in $TS1_A$ [right]) are extracted to further understand the overlap. The energy gap between bonding (HOMO-4 in $TS1_D$ and HOMO in $TS1_A$) and antibonding orbitals (LUMO in $TS1_D$ and LUMO+1 in $TS1_A$) is lower by 2.09 eV in $TS1_A$ than in $TS1_D$. This outcome from frontier MOs is qualitatively consistent with the barrier heights of the two pathways, which shows that the $TS1_A$ lies ~1.4 kcal/mol lower than that of $TS1_D$ (in both THF and MeCN).

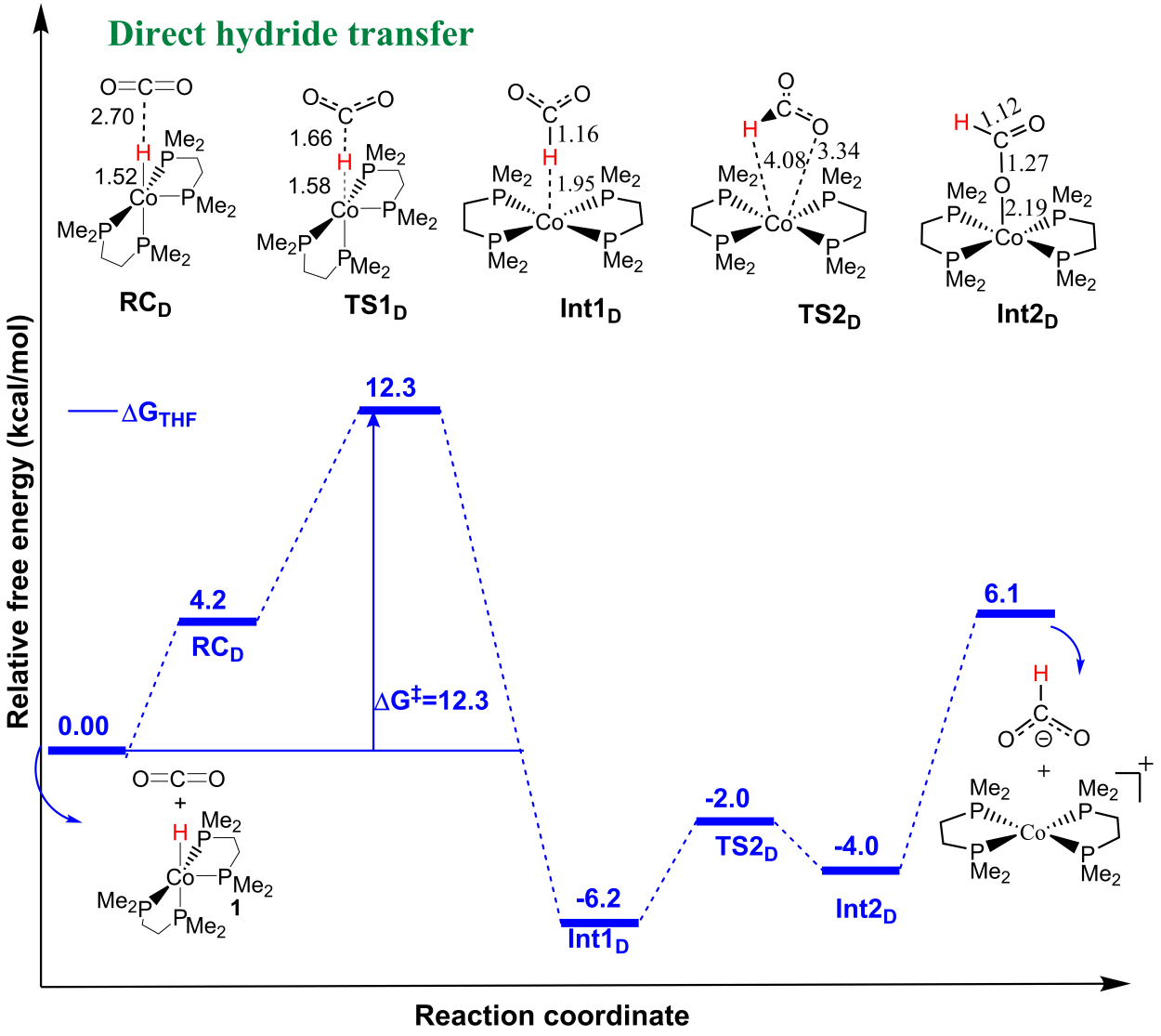

Figure S7. Free energy profile of *direct hydride transfer* pathway relative to the energy of $Co(dmpe)_2H$ and CO_2 calculated using M06 with Co-(SDD) and 6-31G* basis set for all the nonmetals (plus additional p functions on the hydride).

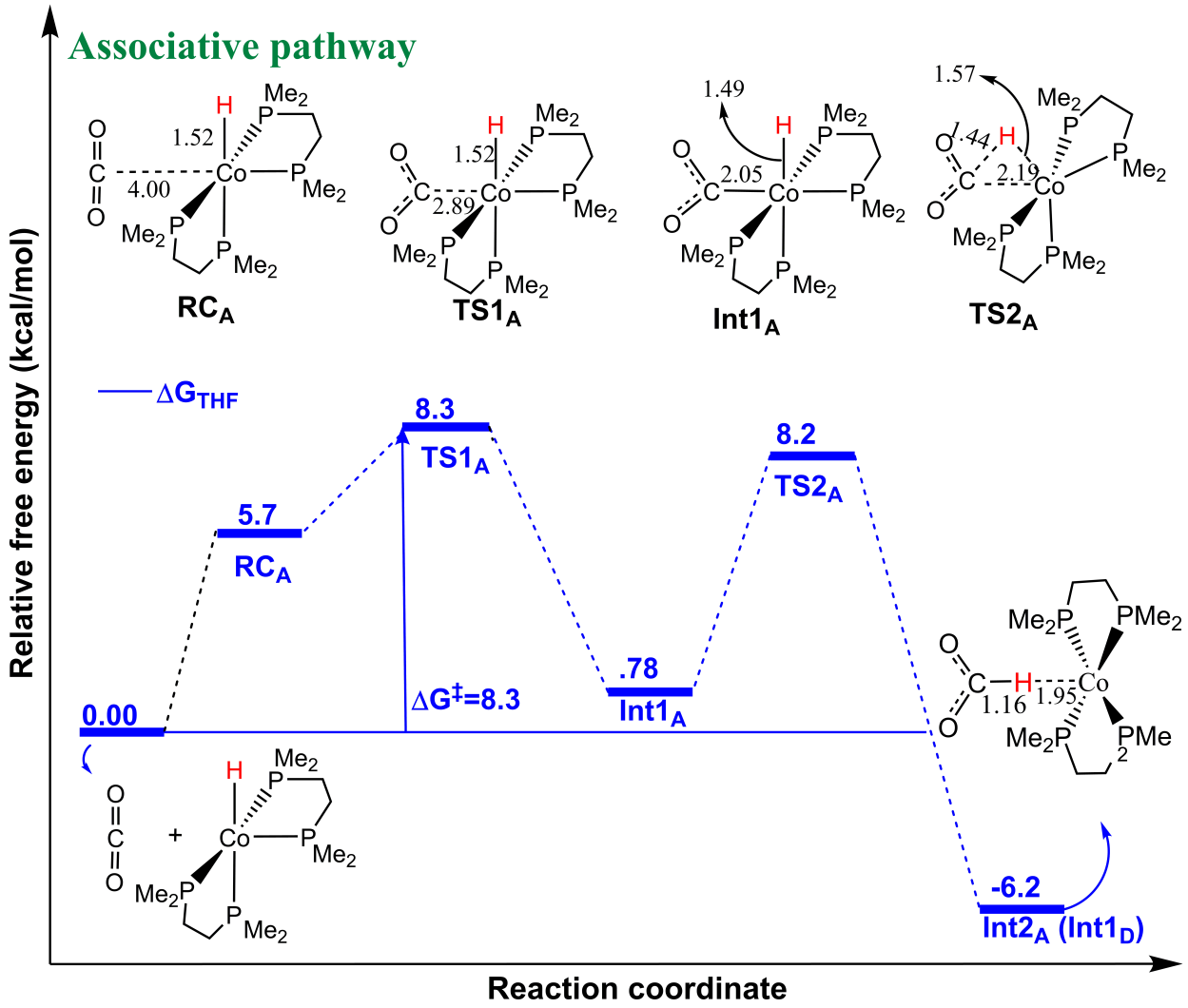

Figure S8. Free energy profile of *associative* pathway relative to the total energy of $Co(dmpe)_2H$ and CO_2, calculated using M06 with Co-(SDD) and 6-31G* basis set for all the nonmetals (plus additional p functions on the hydride).

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Optimized structures (in THF) in XYZ format:

$Co(dmpe)_2H$ or 1

50

H	0.627686000	0.406429000	-1.573076000
Co	0.157028000	-0.034105000	-0.225574000
P	1.588766000	1.483962000	0.377433000
P	-1.341198000	1.459768000	-0.710840000
P	0.333081000	-1.936724000	-1.178965000
P	-0.468331000	-1.087509000	1.576111000
C	3.078662000	1.782984000	-0.678149000
C	0.693496000	3.122064000	0.212796000
C	-0.370954000	3.047632000	-0.878714000
C	-2.247244000	1.451915000	-2.321971000
C	-0.537662000	-2.231553000	-2.781011000
C	-2.253464000	-1.134279000	2.059733000
C	-2.718581000	2.009345000	0.397870000
C	2.376223000	1.724954000	2.033997000
C	-0.122091000	-2.907025000	1.351536000
C	-0.370116000	-3.285093000	-0.103913000
C	0.269689000	-0.808792000	3.244864000
C	1.996111000	-2.618804000	-1.626813000
H	-0.724351000	-3.504487000	2.045963000
H	0.931383000	-3.064702000	1.612820000
H	-1.446540000	-3.321673000	-0.310750000
H	0.047750000	-4.266414000	-0.355885000
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H	1.616461000	1.725584000	2.819437000
H	3.075236000	0.907622000	2.235515000
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H	-3.209390000	2.911760000	0.016354000
H	-3.468256000	1.217496000	0.482293000

RC_D

53

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P	-0.437295000	-1.339650000	-1.512415000
P	0.388218000	2.162809000	-0.035153000
P	2.418979000	-0.018807000	-0.008737000

C	-1.875586000	-0.787111000	2.604501000
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H	3.296868000	-2.102907000	0.923991000
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C	-4.387927000	1.132935000	-0.118764000
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O	-4.686588000	0.072805000	-0.505678000

$TS1_D$

53

H	-0.681518000	1.335044000	-0.458388000
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H	2.960198000	3.131664000	1.130784000
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C	-1.520243000	2.805179000	-0.589974000
O	-0.761333000	3.605002000	-0.145706000
O	-2.556261000	2.482445000	-1.078232000

Int1$_D$

53

H	-0.344017000	0.939865000	-1.215012000
Co	0.118648000	-0.282766000	0.118037000
P	-1.277481000	0.506145000	1.626288000
P	-1.580859000	-1.497549000	-0.563139000
P	1.808102000	0.985780000	0.747355000
P	1.604841000	-1.490933000	-0.928259000
C	-1.547393000	2.324003000	1.733482000
C	-3.006935000	-0.122094000	1.310139000
C	-3.114850000	-0.562053000	-0.142955000
C	-1.815807000	-1.853834000	-2.347838000
C	1.791303000	2.753095000	0.252849000
C	1.825195000	-1.164500000	-2.727055000
C	-1.884939000	-3.148177000	0.194319000
C	-1.073354000	0.070666000	3.404115000
C	3.290848000	-1.108213000	-0.260813000
C	3.373060000	0.398385000	-0.066292000
C	1.602159000	-3.330218000	-0.899474000
C	2.310210000	1.095732000	2.514513000
H	4.072243000	-1.485704000	-0.929715000

H	3.388542000	-1.631315000	0.697562000
H	3.432475000	0.905459000	-1.036134000
H	4.249183000	0.701741000	0.516394000
H	0.951301000	-1.527754000	-3.273720000
H	1.895066000	-0.088199000	-2.900540000
H	2.718848000	-1.662034000	-3.117765000
H	2.524747000	-3.722372000	-1.339776000
H	1.522205000	-3.689591000	0.129813000
H	0.758340000	-3.721091000	-1.473253000
H	2.427405000	0.094944000	2.937873000
H	1.547649000	1.627484000	3.088151000
H	3.254926000	1.639716000	2.613387000
H	1.527706000	2.814737000	-0.806784000
H	2.774138000	3.206931000	0.416791000
H	1.047819000	3.310789000	0.825857000
H	-1.059265000	-2.556241000	-2.706878000
H	-1.733149000	-0.923083000	-2.914024000
H	-2.804291000	-2.289069000	-2.526200000
H	-0.652733000	2.816961000	2.122437000
H	-1.755664000	2.717475000	0.734949000
H	-2.385399000	2.559191000	2.397401000
H	-3.113645000	0.308193000	-0.810263000
H	-4.015642000	-1.154920000	-0.336799000
H	-3.739942000	0.651335000	1.561045000
H	-3.182623000	-0.966350000	1.986326000
H	-1.938049000	0.412513000	3.982703000
H	-0.982939000	-1.013772000	3.506695000
H	-0.173305000	0.527457000	3.820216000
H	-1.904713000	-3.065004000	1.283997000
H	-2.836866000	-3.567482000	-0.147863000
H	-1.080322000	-3.837858000	-0.071581000
C	-0.646400000	1.687957000	-2.054358000

O	-1.870579000	1.928249000	-2.136713000
O	0.299140000	2.131609000	-2.740619000

$TS2_D$

53

H	-0.500404000	2.365223000	-2.454232000
Co	0.181655000	-0.377721000	0.171898000
P	-1.258372000	0.281987000	1.683788000
P	-1.512823000	-1.303414000	-0.862706000
P	1.834432000	0.914521000	0.783077000
P	1.709643000	-1.611900000	-0.769879000
C	-1.702191000	2.045518000	1.939079000
C	-2.909317000	-0.506882000	1.350562000
C	-3.086650000	-0.634592000	-0.156803000
C	-1.733674000	-1.033898000	-2.660806000
C	1.915677000	2.326969000	-0.386973000
C	1.704729000	-2.335138000	-2.460083000
C	-1.746753000	-3.124053000	-0.703697000
C	-0.911606000	-0.270995000	3.404840000
C	3.372798000	-0.785368000	-0.735094000
C	3.466837000	0.065605000	0.525144000
C	1.994286000	-3.105548000	0.271753000
C	2.104706000	1.731870000	2.405901000
H	3.434606000	-0.155625000	-1.629830000
H	4.176967000	-1.526272000	-0.799740000
H	4.279866000	0.797794000	0.472169000
H	3.645966000	-0.563040000	1.405106000
H	0.844127000	-2.994156000	-2.597008000
H	1.653540000	-1.536699000	-3.204882000
H	2.616118000	-2.917252000	-2.630472000
H	2.848171000	-3.682465000	-0.098916000

H	2.186473000	-2.807193000	1.305673000
H	1.104631000	-3.740407000	0.263803000
H	2.167061000	0.983984000	3.200649000
H	1.284775000	2.417209000	2.631472000
H	3.037568000	2.304524000	2.391462000
H	2.054743000	1.948286000	-1.403231000
H	2.750426000	2.991490000	-0.139095000
H	0.971618000	2.883342000	-0.366386000
H	-0.863764000	-1.387948000	-3.217898000
H	-1.871398000	0.040113000	-2.829410000
H	-2.622393000	-1.566704000	-3.015229000
H	-0.848515000	2.589155000	2.352128000
H	-1.956256000	2.511699000	0.982680000
H	-2.540377000	2.133064000	2.637796000
H	-3.221629000	0.351031000	-0.617216000
H	-3.944297000	-1.260683000	-0.426733000
H	-3.715436000	0.069127000	1.817244000
H	-2.896490000	-1.495782000	1.824499000
H	-1.774313000	-0.081030000	4.052073000
H	-0.689196000	-1.341513000	3.412738000
H	-0.048330000	0.262545000	3.809903000
H	-1.783612000	-3.408682000	0.351396000
H	-2.676772000	-3.438802000	-1.188507000
H	-0.913998000	-3.656596000	-1.170545000
C	-1.384809000	2.662341000	-1.824904000
O	-1.156752000	3.511211000	-0.928315000
O	-2.476355000	2.115989000	-2.119374000

PC

53

H	-0.923505000	2.855920000	-2.886841000
Co	0.001055000	0.028489000	-0.161085000
P	-1.225965000	0.261856000	1.629576000
P	-1.679772000	-1.144919000	-0.967680000
P	1.691443000	1.286735000	0.515253000
P	1.512599000	-1.459815000	-0.664697000
C	-1.746742000	1.903341000	2.303118000
C	-2.901370000	-0.538520000	1.379644000
C	-3.215948000	-0.574069000	-0.110764000
C	-2.093601000	-1.003041000	-2.749457000
C	2.234181000	2.572421000	-0.686172000
C	1.651686000	-2.243993000	-2.333215000
C	-1.806587000	-2.968622000	-0.729330000
C	-0.713971000	-0.546454000	3.214496000
C	3.224496000	-0.749178000	-0.492120000
C	3.218341000	0.239951000	0.664098000
C	1.675400000	-2.965296000	0.400369000
C	1.788100000	2.266324000	2.070317000
H	3.455594000	-0.236428000	-1.433206000
H	3.968252000	-1.542910000	-0.358316000
H	4.118683000	0.864523000	0.688937000
H	3.156302000	-0.287605000	1.623559000
H	0.794801000	-2.896530000	-2.523331000
H	1.660139000	-1.465477000	-3.101247000
H	2.564680000	-2.843066000	-2.422879000
H	2.483865000	-3.622865000	0.060392000
H	1.877819000	-2.656906000	1.430209000
H	0.740734000	-3.530672000	0.401206000
H	1.534652000	1.653892000	2.938779000
H	1.100524000	3.113695000	2.020153000
H	2.802631000	2.655518000	2.206310000
H	2.381065000	2.134405000	-1.675172000

H	3.169293000	3.034203000	-0.352678000
H	1.466906000	3.345236000	-0.766926000
H	-1.309107000	-1.473072000	-3.349240000
H	-2.144887000	0.050633000	-3.026402000
H	-3.047708000	-1.492510000	-2.968545000
H	-0.876821000	2.476764000	2.629322000
H	-2.247733000	2.472163000	1.518146000
H	-2.422617000	1.782899000	3.156849000
H	-3.430843000	0.432706000	-0.485400000
H	-4.073525000	-1.215658000	-0.344460000
H	-3.669747000	-0.007076000	1.951034000
H	-2.848739000	-1.557398000	1.781178000
H	-1.484946000	-0.459505000	3.988798000
H	-0.509452000	-1.605358000	3.033149000
H	0.206114000	-0.087942000	3.588120000
H	-1.705927000	-3.221558000	0.329315000
H	-2.772913000	-3.337602000	-1.088487000
H	-1.016676000	-3.485069000	-1.280072000
C	-0.868819000	2.412820000	-1.862503000
O	-1.362892000	3.067118000	-0.929325000
O	-0.289523000	1.282759000	-1.834159000

RC_A

53

Co	-0.349736000	0.076880000	-0.070260000
P	-1.908000000	1.561862000	-0.307741000
P	1.157953000	1.574272000	0.286717000
P	-0.708916000	-1.900297000	0.632572000
P	0.057099000	-0.779233000	-2.021452000
C	-3.181746000	1.714704000	1.025355000

C	-1.055070000	3.226627000	-0.190793000
C	0.191675000	3.131009000	0.684828000
C	2.295215000	1.527038000	1.744097000
C	0.205597000	-2.608130000	2.074312000
C	1.807408000	-1.024850000	-2.572021000
C	2.352921000	2.217495000	-0.975030000
C	-3.005588000	1.882795000	-1.765265000
C	-0.592704000	-2.526872000	-2.048884000
C	-0.355971000	-3.171177000	-0.687682000
C	-0.650393000	-0.146132000	-3.606346000
C	-2.430351000	-2.338354000	1.157283000
H	-0.568155000	0.371255000	1.376458000
H	-0.144700000	-3.102244000	-2.867738000
H	-1.667695000	-2.450295000	-2.252354000
H	0.698414000	-3.452835000	-0.580407000
H	-0.954398000	-4.079103000	-0.548863000
H	2.263433000	-0.056514000	-2.796006000
H	2.385272000	-1.491728000	-1.770036000
H	1.867581000	-1.649925000	-3.469905000
H	-0.396318000	-0.800902000	-4.447383000
H	-1.738822000	-0.083562000	-3.529195000
H	-0.261584000	0.854357000	-3.817446000
H	-3.120814000	-2.163269000	0.327616000
H	-2.725971000	-1.684145000	1.983176000
H	-2.520579000	-3.380146000	1.486396000
H	1.280538000	-2.552630000	1.881820000
H	-0.069667000	-3.650249000	2.273564000
H	-0.012803000	-2.011550000	2.964763000
H	3.075667000	0.780209000	1.571135000
H	1.729326000	1.233328000	2.632098000
H	2.774118000	2.495787000	1.929334000
H	-3.832816000	0.835250000	1.012790000

H	-2.688204000	1.750467000	2.000312000
H	-3.801250000	2.610959000	0.905783000
H	-0.094553000	3.051840000	1.740698000
H	0.823619000	4.021903000	0.585414000
H	-1.741435000	4.004712000	0.166518000
H	-0.772980000	3.496402000	-1.216886000
H	-3.608025000	2.788192000	-1.627619000
H	-2.407076000	1.998352000	-2.672369000
H	-3.681708000	1.034488000	-1.910400000
H	1.831002000	2.460384000	-1.905083000
H	2.871049000	3.115875000	-0.620763000
H	3.103810000	1.453629000	-1.195506000
C	3.240565000	-1.244523000	3.966541000
O	2.519701000	-0.854999000	4.797361000
O	3.969153000	-1.644834000	3.147200000

$TS1_A$

53

Co	-0.099552000	0.029416000	0.247066000
P	-1.803015000	1.374271000	-0.143489000
P	1.234281000	1.739924000	0.426811000
P	-0.795551000	-1.945744000	0.790245000
P	0.361219000	-0.783724000	-1.743707000
C	-2.988745000	1.630897000	1.250804000
C	-1.092723000	3.088153000	-0.331570000
C	0.121918000	3.238329000	0.572861000
C	2.361625000	2.116423000	1.842585000
C	-0.299370000	-2.944932000	2.264417000
C	2.083374000	-1.243770000	-2.226292000
C	2.341749000	2.261998000	-0.959196000

C	-3.023564000	1.401127000	-1.537208000
C	-0.520874000	-2.416866000	-1.911108000
C	-0.459264000	-3.159230000	-0.582702000
C	-0.162289000	0.032119000	-3.315669000
C	-2.628874000	-2.107564000	0.994209000
H	-0.365222000	0.355642000	1.677776000
H	-0.104728000	-3.005027000	-2.737175000
H	-1.561229000	-2.182880000	-2.166855000
H	0.547828000	-3.558509000	-0.415198000
H	-1.157568000	-4.003598000	-0.547711000
H	2.702594000	-0.345702000	-2.301059000
H	2.525081000	-1.892623000	-1.469878000
H	2.091037000	-1.755074000	-3.194749000
H	0.179877000	-0.535163000	-4.187751000
H	-1.251564000	0.101419000	-3.354392000
H	0.248882000	1.043677000	-3.378482000
H	-3.139175000	-1.709942000	0.113147000
H	-2.943703000	-1.521859000	1.863128000
H	-2.937390000	-3.147895000	1.146722000
H	0.759240000	-3.209733000	2.215388000
H	-0.887121000	-3.867814000	2.323564000
H	-0.463885000	-2.365341000	3.176413000
H	3.273761000	1.516592000	1.781259000
H	1.864318000	1.890521000	2.788301000
H	2.647622000	3.174501000	1.834717000
H	-3.600150000	0.733908000	1.382947000
H	-2.438131000	1.799270000	2.179593000
H	-3.654541000	2.481424000	1.066527000
H	-0.189335000	3.287711000	1.623488000
H	0.684139000	4.154788000	0.357334000
H	-1.850452000	3.855764000	-0.132925000
H	-0.794921000	3.189058000	-1.383315000

H	-3.739453000	2.222628000	-1.420952000
H	-2.509817000	1.531771000	-2.492350000
H	-3.582335000	0.461163000	-1.575553000
H	1.786581000	2.281831000	-1.900995000
H	2.765897000	3.256544000	-0.782184000
H	3.164924000	1.550317000	-1.061844000
C	2.371186000	-1.107090000	1.694631000
O	2.036461000	-0.903116000	2.809578000
O	3.058047000	-1.466494000	0.799796000

Int1$_A$

53

Co	0.090082000	-0.018914000	0.340069000
P	-1.670906000	1.388470000	0.000678000
P	1.363179000	1.756089000	0.478823000
P	-0.951201000	-1.893411000	0.734773000
P	0.472896000	-0.860540000	-1.727991000
C	-2.696011000	1.624667000	1.511172000
C	-0.962238000	3.088461000	-0.227484000
C	0.267971000	3.243761000	0.657177000
C	2.506131000	1.971092000	1.893736000
C	-1.023125000	-2.540058000	2.442539000
C	2.046524000	-0.681237000	-2.660992000
C	2.450625000	2.244595000	-0.921145000
C	-2.998768000	1.395414000	-1.280676000
C	0.214580000	-2.718252000	-1.643531000
C	-0.091995000	-3.216005000	-0.229583000
C	-0.689633000	-0.442079000	-3.101290000
C	-2.698728000	-2.099801000	0.192056000
H	-0.202081000	0.341439000	1.729432000

H	1.100574000	-3.216844000	-2.046502000
H	-0.616455000	-2.951469000	-2.317585000
H	0.836205000	-3.425576000	0.306740000
H	-0.690034000	-4.133934000	-0.245996000
H	2.120495000	0.325384000	-3.079747000
H	2.880815000	-0.866936000	-1.987075000
H	2.068540000	-1.399001000	-3.487323000
H	-0.459114000	-1.030124000	-3.996193000
H	-1.722724000	-0.646654000	-2.810340000
H	-0.604857000	0.617752000	-3.358859000
H	-2.789298000	-1.923623000	-0.883329000
H	-3.346381000	-1.391229000	0.714464000
H	-3.052039000	-3.113296000	0.408912000
H	-0.026065000	-2.452894000	2.878273000
H	-1.361315000	-3.580484000	2.460661000
H	-1.713523000	-1.929533000	3.031601000
H	3.335608000	1.266026000	1.814696000
H	1.981010000	1.776526000	2.830714000
H	2.902255000	2.991609000	1.903123000
H	-3.226674000	0.700897000	1.757392000
H	-2.047900000	1.864790000	2.357378000
H	-3.429697000	2.426325000	1.376815000
H	-0.021623000	3.296150000	1.712846000
H	0.826838000	4.157584000	0.427452000
H	-1.717219000	3.854256000	-0.016039000
H	-0.688061000	3.181679000	-1.285645000
H	-3.662329000	2.253328000	-1.129315000
H	-2.573528000	1.457892000	-2.284044000
H	-3.596080000	0.482641000	-1.212543000
H	1.858569000	2.383557000	-1.829584000
H	2.974532000	3.179452000	-0.696716000
H	3.190222000	1.462480000	-1.104638000

C	1.693994000	-1.005345000	1.064061000
O	1.820918000	-1.112339000	2.306755000
O	2.494138000	-1.461242000	0.200828000

$TS2_A$

53

Co	0.153030000	-0.032775000	0.341930000
P	-1.650514000	1.257877000	0.216354000
P	1.286069000	1.892893000	0.376193000
P	-0.981400000	-1.911930000	0.728945000
P	0.549234000	-0.804886000	-1.701273000
C	-2.503520000	1.829048000	1.750174000
C	-1.134067000	2.863563000	-0.553846000
C	0.139026000	3.338463000	0.125181000
C	2.098732000	2.397688000	1.944342000
C	-0.780966000	-2.730736000	2.356754000
C	2.256185000	-1.309962000	-2.178101000
C	2.598487000	2.213916000	-0.867713000
C	-3.124599000	0.888374000	-0.835587000
C	-0.390003000	-2.404239000	-1.897825000
C	-0.470543000	-3.140138000	-0.561395000
C	0.049185000	0.083315000	-3.240322000
C	-2.815173000	-2.034471000	0.582096000
H	0.907410000	-0.350549000	1.657209000
H	0.065351000	-3.025469000	-2.677154000
H	-1.395207000	-2.135438000	-2.246350000
H	0.511081000	-3.514373000	-0.263558000
H	-1.173854000	-3.979561000	-0.599875000
H	2.908902000	-0.434362000	-2.216839000
H	2.654499000	-1.997528000	-1.429185000

H	2.261081000	-1.797389000	-3.158799000
H	0.196194000	-0.540688000	-4.128523000
H	-1.003528000	0.373520000	-3.188171000
H	0.647353000	0.991482000	-3.358046000
H	-3.150090000	-1.814316000	-0.432987000
H	-3.308796000	-1.349751000	1.276122000
H	-3.124698000	-3.054576000	0.831728000
H	0.274095000	-2.725923000	2.626500000
H	-1.150570000	-3.760827000	2.323683000
H	-1.357109000	-2.174549000	3.102362000
H	2.911120000	1.705634000	2.162462000
H	1.369521000	2.358621000	2.757959000
H	2.487079000	3.418293000	1.862057000
H	-2.901057000	0.961486000	2.284735000
H	-1.784850000	2.319109000	2.412326000
H	-3.325538000	2.519818000	1.532249000
H	-0.093697000	3.743124000	1.116371000
H	0.642592000	4.133363000	-0.435076000
H	-1.941834000	3.602417000	-0.491733000
H	-0.959247000	2.655463000	-1.616120000
H	-3.593952000	1.826245000	-1.150381000
H	-2.835961000	0.326491000	-1.727329000
H	-3.867945000	0.310984000	-0.284399000
H	2.168982000	2.221124000	-1.873232000
H	3.081183000	3.180118000	-0.688242000
H	3.343248000	1.420346000	-0.798673000
C	1.962356000	-0.991833000	1.048223000
O	1.912392000	-2.236540000	1.165325000
O	2.983130000	-0.272860000	0.968738000

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53

H	-0.344017000	0.939865000	-1.215012000
Co	0.118648000	-0.282766000	0.118037000
P	-1.277481000	0.506145000	1.626288000
P	-1.580859000	-1.497549000	-0.563139000
P	1.808102000	0.985780000	0.747355000
P	1.604841000	-1.490933000	-0.928259000
C	-1.547393000	2.324003000	1.733482000
C	-3.006935000	-0.122094000	1.310139000
C	-3.114850000	-0.562053000	-0.142955000
C	-1.815807000	-1.853834000	-2.347838000
C	1.791303000	2.753095000	0.252849000
C	1.825195000	-1.164500000	-2.727055000
C	-1.884939000	-3.148177000	0.194319000
C	-1.073354000	0.070666000	3.404115000
C	3.290848000	-1.108213000	-0.260813000
C	3.373060000	0.398385000	-0.066292000
C	1.602159000	-3.330218000	-0.899474000
C	2.310210000	1.095732000	2.514513000
H	4.072243000	-1.485704000	-0.929715000
H	3.388542000	-1.631315000	0.697562000
H	3.432475000	0.905459000	-1.036134000
H	4.249183000	0.701741000	0.516394000
H	0.951301000	-1.527754000	-3.273720000
H	1.895066000	-0.088199000	-2.900540000
H	2.718848000	-1.662034000	-3.117765000
H	2.524747000	-3.722372000	-1.339776000
H	1.522205000	-3.689591000	0.129813000
H	0.758340000	-3.721091000	-1.473253000
H	2.427405000	0.094944000	2.937873000
H	1.547649000	1.627484000	3.088151000

H	3.254926000	1.639716000	2.613387000
H	1.527706000	2.814737000	-0.806784000
H	2.774138000	3.206931000	0.416791000
H	1.047819000	3.310789000	0.825857000
H	-1.059265000	-2.556241000	-2.706878000
H	-1.733149000	-0.923083000	-2.914024000
H	-2.804291000	-2.289069000	-2.526200000
H	-0.652733000	2.816961000	2.122437000
H	-1.755664000	2.717475000	0.734949000
H	-2.385399000	2.559191000	2.397401000
H	-3.113645000	0.308193000	-0.810263000
H	-4.015642000	-1.154920000	-0.336799000
H	-3.739942000	0.651335000	1.561045000
H	-3.182623000	-0.966350000	1.986326000
H	-1.938049000	0.412513000	3.982703000
H	-0.982939000	-1.013772000	3.506695000
H	-0.173305000	0.527457000	3.820216000
H	-1.904713000	-3.065004000	1.283997000
H	-2.836866000	-3.567482000	-0.147863000
H	-1.080322000	-3.837858000	-0.071581000
C	-0.646400000	1.687957000	-2.054358000
O	-1.870579000	1.928249000	-2.136713000
O	0.299140000	2.131609000	-2.740619000