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APPLICATION OF LOW VALENT MAIN GROUP ELEMENTS IN SMALL MOLECULE ACTIVATION REACTIONS



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Abstract

Exceptional synthetic transformations have been achieved through the years by the use of transition metal catalysts. On the contrary, only a few industrialized processes use main group based catalysts due to its low reactivity and poor recovery from the reaction media. In this thesis, a detailed computational study of the application of main group elements acting as transition metals for the activation of small molecules is presented. The hydroboration of CO₂ by group 14 NacNac derived systems and the activation of H₂ by low valent aluminum species are studied. Low valent main group 14 elements (Si, Ge, Sn, and Pb) bearing charge 2+ and a N-Arylisopropyl- β -diketiiminate ligand were used for the transformation of CO₂, aimed to yield in subsequent steps formic acid derivatives. It has been found that when going down in group 14, the reaction becomes more favored. This study suggests that Pb(II) is a preponderate candidate for hydroboration of CO₂. We hope this study motivates future experimental work on main group catalysis, especially using low valent lead compounds. On the other hand, for the activation of H₂ by aluminyll anions, it was found that the potassium atoms that help stabilize the dimeric form of the catalysts do not play a catalytic role in the activation of the gas. To explore substituent effect in geometry, electronic structure, and reactivity, simple AlR₁R₂⁻ species were used as a model. High-level coupled-cluster geometry and energetics were obtained for each structure. In conclusion, donation and back-donation effects were found in these structures, resembling a TM behavior. Moreover, monosubstituted aluminyll anions reported lower activation energies concerning the disubstituted systems.

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Contents

Abstract	i
Acknowledgements	ii
List of Figures	vii
List of Tables	xiii
Abbreviations	xv
Physical Constants	xvii
Symbols	xviii
1 General Introduction	1
2 Activation and Hydroboration of CO ₂ by Low Valent Main Group Catalysts	5
2.1 Introduction	6
2.2 Computational Details	10
2.3 Results and Discussion	12
2.3.1 Starting the Catalytic Cycle: The CO ₂ Activation Step	12
2.3.1.1 The Reactant Complex	18
2.3.1.2 CO ₂ Activation	19
2.3.1.3 Conformational Analysis	26
2.3.2 Completing the Catalytic Cycle: The Hydroboration Step	30
2.3.2.1 Analysis of Reaction Pathways	33
2.3.2.2 Characterization of INT _{2-Oo} ^{LA} and INT _{2-Oo}	44
2.4 Conclusions	50
3 Activation of H ₂ by Aluminyll Anions	52
3.1 Introduction	53
3.2 Theoretical Methods	55
3.3 Results and Discussion	59

3.3.1	The Mechanism of H ₂ Activation by the [K{Al(NON)}] ₂ Aluminyl Anions: Do the Potassium Atoms Play any Catalytic Role?	59
3.3.2	Substituent Effect in the Activation of H ₂ by Simple Aluminyl Anions	64
3.3.2.1	Orbital Interactions	65
3.3.2.2	Molecular Geometries of Aluminyl Anions	69
3.3.2.3	H ₂ Activation	72
3.3.2.4	Symmetry-Adapted Perturbation Theory Analysis	75
3.3.2.5	Structural Analysis of Products of Activation: The AlH ₂ R ₁ R ₂ Species	80
3.4	Conclusions	83
A	Theoretical Tools	85
A.1	Symmetry-Adapted Perturbation Theory	85
A.2	Energy Profiles and Reaction Force	88
A.3	Reaction Electronic Flux	91
A.4	Noncovalent Interaction Index	93
B	Symmetry-Adapted Reaction Electronic Flux in Cycloaddition Reactions	95
B.1	General Introduction	95
B.2	Theory	97
B.3	Butadiene plus Ethylene and Diacetylene with Ethylene Reactions	101
B.3.1	Computational Details	102
B.3.2	Results and Discussions	103
B.3.2.1	Energy and Reaction Force Analysis	103
B.3.2.2	Symmetry Adapted Reaction Electronic Flux	106
B.3.3	Conclusions	114
B.4	Decomposition of the Electronic Activity in Competing [5,6] and [6,6] Cycloaddition Reactions Between C ₆₀ and Cyclopentadiene	115
B.4.1	Computational Details	117
B.4.2	Results and Discussion	118
B.4.2.1	Symmetry-Adapted Reaction Electronic Flux	122
B.4.2.2	Symmetry-Adapted Kinetic Energy	127
B.4.3	Conclusions	129
B.5	Concluding Remarks	131
C	Gibbs Free Energies: The quasi-RRHO method	132
D	Relativistic Effects	137
D.1	Theory	137
D.1.1	Douglas-Kroll-Hess Approximation	138
D.2	Results and Discussion	139

D.2.1	Energetic Comparison	139
D.2.2	Relativistic Effects on Frontier Molecular Orbitals	141
E	Benchmark $\text{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\text{INT}_{2-\text{Oo}}$	143
F	Symmetry-Adapted Reaction Electronic Flux in Cycloaddition Reactions	145
G	Energies for the Activation of H_2 by Alumanyl Anions	150
G.1	Activation Enthalpies	150
G.2	Reaction Enthalpies	151
H	Bibliography	152

List of Figures

1.1	Energy profile for kinetic and thermodynamic stability in non-bulky and bulky low valent MG compounds.	3
2.1	Catalytic cycle for the hydroboration/reduction of CO ₂	8
2.2	CO ₂ activation by the main group Si ^(II) (1), Ge ^(II) (2), Sn ^(II) (3) and Pb ^(II) (4) based catalyst. CO ₂ insertion in the E –H bond is schematized in color-code.	13
2.3	Approaches of CO ₂ to the 1-4 MG-complexes. For the sake of clarity hydrogen atoms attached to carbons and Ar =2,6–iPr ₂ C ₆ H ₃ are omitted from the molecular representations. Oxygens are in red, nitrogens are in blue, carbons are in grey, and hydride is colored in white.	14
2.4	Molecular electrostatic potential of complexes 1-4 and CO ₂	15
2.5	HOMO-LUMO densities and dual descriptor computed for complexes 1-4 and CO ₂ molecule (isovalue 0.01 a.u.). For dual descriptor, nucleophilic and electrophilic zones are represented in red and green, respectively. Hydrogen atoms attached to carbons were omitted for clarity.	16
2.6	Contribution from main group element (E), hydride (H) and Nac–Nac ligand (L) to the HOMO orbital.	17
2.7	SAPT0 results for the reactant complex in the (2 + CO ₂)@ R1 reaction pathway.	18
2.8	SAPT0 along the reaction coordinate for (2 + CO ₂)@ R1 and (2 + CO ₂)@ R2 reaction pathway.	19
2.9	Transition state structures for both front- and back-side approaches (R1 and R2), respectively. Hydrogens attached to carbons and Ar =2,6–iPr ₂ C ₆ H ₃ are omitted from the molecular representations. Bond distances and angles are in (Å) and degrees (°), respectively.	21
2.10	Linear relationship between activation energies ($\Delta E^\ddagger$) and bond polarity index ($\Delta Q_{\mathbf{E}-\mathbf{H}}$) for complexes studied including silicon for the R1 and R2 pathways (R1 , $\Delta E^\ddagger = -38.6\Delta Q_{\mathbf{E}-\mathbf{H}} + 60.5$; R2 , $\Delta E^\ddagger = -33.7\Delta Q_{\mathbf{E}-\mathbf{H}} + 53.8$)	23

2.11	Representation of the conformational stereoisomers obtained as products of the reactions between complexes 1-4 and CO ₂ . The products from both approaches (R1 and R2) are named PE_H<i>i</i> and PE_H<i>o</i> , respectively. The free torsion around the C–O bond (green arrow) afford the more stable complexes PE_O<i>i</i> and PE_O<i>o</i> , respectively. Other possible interconversions are also shown by rotating the M–O bond (magenta and turquoise arrows). E–O torsion in magenta was found to be not possible. The bidentated NacNac ligand was schematized by connected nitrogen atoms (blue).	27
2.12	Potential energy surface (in kcal mol ⁻¹) for the front- and back-side reactions of MG-hydride complexes with CO ₂ ; (a) silicon, (b) germanium, (c) tin and (d) lead. Interconversion to different conformational stereoisomers are also shown: torsion around C–O and E–O bonds. Note that displayed values are relative to the E + CO ₂ isolated reactants. All energies are given in kcal mol ⁻¹ , computed in toluene and corrected with zero point energies.	28
2.13	Hydroboration of formates with HBpin reagent. Bond insertions are schematized in color-code.	31
2.14	Relevant low valent Ge and Sn compounds.	32
2.15	Resume of occurrence of reactions with HBpin (top). Schematic representation of steric repulsions in PE_O<i>i</i> + HBpin system (bottom left) and TS structure for the non-methylated HBpin with PE_O<i>i</i> .	33
2.16	Energy profile for the reaction between CO ₂ and HBpin. Gibbs free energies in toluene are reported in kcal mol ⁻¹ .	35
2.17	Gibbs energy profile for the catalytic hydroboration of CO ₂ by the low valent Si catalyst (1). Si-R1/Oo and Si-R2/Ho pathways are represented in black and red, respectively. Energies are reported in kcal mol ⁻¹ using toluene as solvent.	36
2.18	Gibbs energy profile for the catalytic hydroboration of CO ₂ by the low valent Ge catalyst (2). Ge-R1/Oo and Ge-R2/Ho pathways are represented in black and red, respectively. Energies are reported in kcal mol ⁻¹ using toluene as solvent.	37
2.19	Schematic representation for the hydroboration of CO ₂ using (a) L ¹ GeH and (b) L ³ GeH. Transition state structures for the hydroboration step for both catalysts are also shown.	39
2.20	Gibbs energy profile for the catalytic hydroboration of CO ₂ by the low valent Sn catalyst (3). Sn-R1/Oo and Sn-R2/Ho pathways are represented in black and red, respectively. Energies are reported in kcal mol ⁻¹ using toluene as solvent.	41
2.21	Gibbs energy profile for the catalytic hydroboration of CO ₂ by the low valent Si catalyst (4). Pb-R1/Oo and Pb-R2/Ho pathways are represented in black and red, respectively. Energies are reported in kcal mol ⁻¹ using toluene as solvent.	42
2.22	(a) Energy profile along B–H bond distance (neutral path) and energy along Ge–H bond (ionic path). For both reaction pathways relevant structures are presented.	45

2.23	Noncovalent interaction (NCI) analysis of intermolecular interactions in color-code.	46
2.24	SAPT0 analysis for INT _{2-Oo} ^{LA} and INT _{2-Oo} intermediates. Energies are given in kcal mol ⁻¹	47
2.25	Radial pair distribution functions to selected bond distances for INT _{2-Oo} ^{LA} and INT _{2-Oo} . A total of 20,000 conformations were used for statistics.	49
3.1	Structures of the different species discussed: (I) aluminyll anion, (II) low valent Al compound Al ₄ X ₄ , (III) low valent NacNacAl complex (NacNac = ArNC(Me)CHC(Me)NAr] ⁻ with Ar = 2,6 - iPr ₂ C ₆ H ₃)[1], (IV) simplest Arduengo-type Al-based compound, (V) Al(III) derivative (basic structure for hypohomodesmotic energy scheme when R = H) and (VI) Al(III) anion compound (basic structure for the isodesmic energy scheme when R = H).	54
3.2	Reaction pathways for complexes D and M toward activation of H ₂ . Noncovalent interaction (NCI) surfaces for complexes D and M	60
3.3	Isosurfaces and energies of the frontier molecular orbitals HOMO and LUMO for complexes D and M	61
3.4	Energy profile for the activation of H ₂ by catalysts D and M . Bond distances and Mayer bond orders (in parenthesis) are reported for transition states. Energies were computed at the DLPNO-CCSD(T)/def2-TZVP and reported in kcal mol ⁻¹	62
3.5	Substituted aluminyll anions studied in this work.	64
3.6	Selected NBO interactions for systems 3 , 4 , 6 , 7 , 8 , and 9 . Substituent→Al and back-donation interactions are schematized in blue and red arrows, respectively. Second order energies are reported in kcal mol ⁻¹	68
3.7	Mono- and di-substituted aluminyll anions under consideration.	69
3.8	Secondary orbital interactions in systems 7 . <i>E</i> ⁽²⁾ energies are shown below each interaction.	70
3.9	Transition state structures for symmetrically substituted aluminyll anions. Bond distances (blue) are reported in Å, while the H–Al–R angle is given in degrees (red).	73
3.10	Transition state structures for unsymmetrically substituted aluminyll anions. Bond distances (blue) are reported in Å, while the H–Al–R angle is given in degrees (red).	74
3.11	Energy profile for the activation of H ₂ by substituted aluminyll anions. Enthalpies ($\Delta H_{0K} = \Delta E_{\text{CBS}} + \Delta_{\text{DBOC}} + \Delta_{\text{core}} + \Delta_{\text{rel}} + \Delta_{\text{ZPVE}}$) are reported in kcal mol ⁻¹	74
3.12	Analysis of activation energies using the distortion/interaction(SAPT) procedure for mono- and di-substituted aluminyll anions.	78
3.13	Identification of different amino- and hydroxy-substituted AlH ₂ R ₁ R ₂ ⁻ tetravalent structures.	80

A.1	Generic energy (a) and reaction force (b) profiles. Reaction regions are represented in color-code: reactant region (light red), transition state region (green) and product region (orange). The quantities ξ_R , ξ_1 , ξ_{TS} , ξ_2 and ξ_P represent the positions of reactants, activated reactants (force minimum), transition state, activated products (force maximum) and products.	91
A.2	2D plot of s against $\text{sign}(\lambda_2) \cdot \rho$ along with 3D molecular maps for the three noncovalent interactions (hydrogen bond, van der Waals and repulsive) exemplified by the water dimer, the methane dimer and bicyclo[2,2,2]heptane.	94
B.1	Schematic representation of 2-fold degenerated densities with the corresponding electronic configuration in the singlet state.	99
B.2	Reactions under study. R1 proceeds through a C_s reaction path while R2 is characterized by proceeding in a C_{2v} symmetry regime.	101
B.3	Energy profiles for R1 and R2 cycloaddition reactions. Values in kcal mol^{-1} . Vertical dashed lines defines the reaction regions that comes out from the reaction force analysis.	105
B.4	Transition state structures for cycloadditions R1 and R2 . Bond distances and angles of the reactant structure for each reaction are given in parenthesis. Bond distances and angles are given in Å and degrees, respectively.	106
B.5	A' and A'' orbital interactions for R1 . The dotted line corresponds to the σ_h molecular plane. System's wave function is shown below the symmetrized orbital approaches.	107
B.6	Total, A' and A'' reaction electronic fluxes $J(\xi)$, $J_{A'}(\xi)$ and $J_{A''}(\xi)$, respectively. Flux values given in $\text{kcal} \cdot \text{mol}^{-1} \cdot (a_0 \text{amu}^{1/2})^{-1}$. Vertical dotted lines corresponds to the minimum and maximum of the reaction force. They divide the reaction coordinate into reactant, transition state and product regions, respectively.	107
B.7	Different orbital approaches belonging to a defined irreducible representation. The dotted lines that bisect the orbital approaches correspond to the C_2 symmetry axis and the $\sigma(xz)$ plane. The system's wave function is shown below the symmetrized orbital approaches. Each irreducible representations is represented in color code.	111
B.8	(a) $J(\xi)$, $J_{ip}(\xi)$ and $J_{op}(\xi)$; (b) $J_{ip}(\xi)$, $J_{A_1}(\xi)$ and $J_{B_2}(\xi)$; (c) $J_{op}(\xi)$, $J_{A_2}(\xi)$ and $J_{B_1}(\xi)$ reaction electronic fluxes for reaction R2 . Flux values given in $\text{kcal} \cdot \text{mol}^{-1} \cdot (a_0 \text{amu}^{1/2})^{-1}$. Vertical dotted lines corresponds to the minimum and maximum of the reaction force.	113
B.9	Two types of bond in fullerene (C_{60}) schematized along with cyclopentadiene. Labeling of the relevant atoms is shown.	116

B.10	Energy (a) and reaction force profiles (b) for the cycloaddition between C_{60} and cyclopentadiene computed in gas phase. The [5,6] and [6,6] reaction is represented in black and red, respectively. Energies computed at the M06-2X/6-31G(d) level of theory. Vertical dashed lines correspond to the minimum and maximum of the reaction force. These vertical lines divide the reaction coordinate into reactant, transition state and product regions, respectively. In the reduced reaction coordinate, $\xi^* = 0$ is the reactant complex and $\xi^* = 1$ is the product complex (both with C_s symmetry).	120
B.11	DLPNO-CCSD(T)/cc-pVTZ energies for the [5,6] and [6,6] paths associated with the cycloaddition between C_{60} and cyclopentadiene. Energetics are in kcal mol ⁻¹	121
B.12	A' and A'' orbital interactions for cycloaddition between fullerene and C_{60} . Only representative p orbitals are shown for C_{60} . The dotted lines represent the σ molecular plane. The system's electronic wave function is shown below the orbital representation.	122
B.13	Total, A' and A'' electron fluxes represented by $J(\xi^*)$, $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$, respectively, for the [5,6] (a) and [6,6] pathway (b). Structures at key points (labeled as RC , I , II , TS , III , IV , and PC) along the reaction coordinate are shown. Distances are given in Angstroms. Vertical dashed lines correspond to the minimum and maximum of the reaction force. The vertical separators divide the reaction coordinate into reactant, transition state and product regions, respectively. In the reduced reaction coordinate, $\xi^* = 0$ is the reactant complex and $\xi^* = 1$ is the product complex (both with C_s symmetry).	123
B.14	Kinetic energies computed for each irreducible representation ($T_{\Gamma_i}(\xi^*)$) along the reaction coordinate. Reported are (a) A' kinetic energy [$T_{A'}(\xi^*)$] and (b) A'' kinetic energy [$T_{A''}(\xi^*)$] for the [5,6] and [6,6] reaction pathways. Vertical dashed lines correspond to the minimum and maximum of the reaction force; they are black and red for the [5,6] and [6,6] paths, respectively. These vertical lines divide the reaction coordinates into reactant, transition state and product regions, respectively. In the reduced reaction coordinate, $\xi^* = 0$ is the reactant complex and $\xi^* = 1$ is the product complex (both with C_s symmetry).	129
C.1	Vibrational, rotational and interpolated entropy as a function of ω_k at $T = 298.15$ K with $\omega_0 = 100$ cm ⁻¹ . The B_{av} term was computed using the eigenvalues of the moment of inertia tensor for each vibrational mode.	135
C.2	Computed entropy as a function of ω_k at $T = 298.15$ K with variable ω_0 in the range [50,300] cm ⁻¹ . B_{av} computed by using the eigenvalues of the moment of inertia tensor for each vibrational mode.	136

D.1	HOMO, LUMO and dual descriptor obtained by using the M06-2X/6-31G(d)/LANL2DZ (a) and the DKH hamiltonian (DKH2 level of theory) (b).	142
F.1	Energy and reaction force profile for each reaction. Energy and reaction force values are given in kcal mol ⁻¹ and kcal mol ⁻¹ ξ ⁻¹ , respectively.	145
F.2	Computed ill-defined chemical potential and reaction electronic flux for each reaction using orbitalary approximation.	146
F.3	Frontier molecular orbitals for R1 in which is clearly depicted the orbital crossing (left). Symmetry-adapted orbitals for R1 (right), note that orbital-crossing is avoided.	146
F.4	Frontier molecular orbitals for R2 , orbital crossings are more exhaustive due higher level of symmetry. Symmetry-adapted orbitals are depicted below.	147
F.5	Computed ill-defined chemical potential and reaction electronic flux using finite difference approximations are showed for R1 . In $EA(\xi)$ and $IP(\xi)$ profiles, the electronic state of the anion and cation, respectively, are showed in color-code. Electronic state for the neutral system is found to be ¹ A'. Note that from the $EA(\xi)$ and $IP(\xi)$ profiles the multi-reference character showed as discontinuities is clearly observed.	148
F.6	Computed ill-defined chemical potential and reaction electronic flux using finite difference approximations are showed R2 . In $EA(\xi)$ and $IP(\xi)$ profiles, the electronic state of the anion and cation, respectively, are showed in color-code. Electronic state for the neutral system is found to be ¹ A ₁ . Note that from the $EA(\xi)$ and $IP(\xi)$ profiles the multi-reference character showed as discontinuities is clearly observed.	149

List of Tables

1.1	Differences between transition metals and main group elements. . .	2
2.1	Interaction energy of fragments at the reactant complex ($E_R = E_{(C\ CO_2)R} - (E_C + E_{CO_2})$), activation ($\Delta E^\ddagger = E_{(C\ CO_2)TS} - (E_C + E_{CO_2})$), reverse activation ($\Delta E_r^\ddagger = E_{(C\ CO_2)TS} - E_{(C\ CO_2)P}$) and reaction energy ($\Delta E^\circ = E_{(C\ CO_2)P} - (E_C + E_{CO_2})$); $E_{(C\ CO_2)R}$, $E_{(C\ CO_2)TS}$ and $E_{(C\ CO_2)P}$ correspond to the energy of the complex-CO ₂ system in the reactant complex, transition state and product, respectively. E_C and E_{CO_2} are energies of the isolated complex and CO ₂ , respectively. $\Delta E^\ddagger$ and ΔE° energies computed using the 6-311+G(d,p) basis set are shown in parenthesis. All electronic energies are referenced to isolated reactants, given in kcal mol ⁻¹ and corrected with zero point energies in toluene.	20
2.2	Activation energies for CO ₂ activation ($\Delta G_{CO_2}^\ddagger$) and hydroboration ($\Delta G_{LA}^\ddagger$, $\Delta G_{Hydrob.}^\ddagger$, and $\Delta G_{HB}^\ddagger$). $\Delta G_{total}^\ddagger$ represents the total activation energy for the whole catalytic cycle from reactants to products in the forward direction. Gibbs free energies in toluene are reported in kcal mol ⁻¹	34
3.1	Incremented focal point table.	57
3.2	$E^{(2)}$ energies from the natural bond orbital analysis. $E_{aluminum}^{(2)}$ is the substituent→Al donation while $E_{BD}^{(2)}$ accounts for back-donation effects. For systems 9-12 , $E_{BD}^{(2)}$ energies for LP(Al)→ $\pi^*(C,N\ bond)$ (left) and LP(Al)→ $\sigma^*(C,N\ bond)$ (right) are reported.	67
3.3	Geometries for tetravalent AlH ₂ R ₁ R ₂ ⁻ species used in the isodesmic scheme computed at the CCSD(T)/aug-cc-pV(T+d)Z (<i>tight(d)</i>) functions on Al level of theory. All bond lengths given in angstrom (Å) and all bond angles in degrees.	82
B.1	Energetic Properties of each reaction. Remember that $\Delta E^\ddagger = W_1 + W_2$. All values in kcal mol ⁻¹	104
B.2	Activation and reaction energies extracted from energy profiles obtained through the IRC procedure in the gas phase at the M06-2X/6-31G(d) level of theory. The reaction works (W_i) computed from the reaction force analysis are also quoted. Energetic values reported in kcal mol ⁻¹	121
D.1	Electronic energies with/without relativistic DKH Hamiltonian . . .	140

E.1	Benchmark computations on $\mathbf{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\mathbf{INT}_{2-\text{Oo}}$ structures. Structures were optimized from the respective M06-2X structure and verified by frequency calculations. The 6-31G(d,p) was used for second-row atoms while LANL2DZ was used for Ge.	143
E.2	Benchmark computations on $\mathbf{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\mathbf{INT}_{2-\text{Oo}}$ structures. Structures were optimized from the respective M06-2X structure and verified by frequency calculations. The 6-31G(d,p) was used for second-row atoms while LANL2DZ was used for Ge.	144
G.1	Activation energies and different energy corrections. Energies are reported in kcal mol ⁻¹	150
G.2	Reaction energies and different energy corrections. Energies are reported in kcal mol ⁻¹	151

Abbreviations

PES	Potential E nergy S urface
RF	Reaction F orce
REF	Reaction E lectronic F lux
DFT	Density F unctional T heory
R	Reactant(s)
RC	Reactant C omplex
INT	IN Termediate
TS	Transition S tate
P	Product(s)
PC	Product C omplex
HOMO	Highest O ccupied Molecular O rbital
LUMO	Lowest U noccupied Molecular O rbital
IRC	Intrinsic R eaction C oordinate
RRC	Reduced R eaction C oordinate
NBO	Natural B ond O rbital
EA	Electronic A ffinity
IP	Ionization P otential
SAPT	Symmetry A dapted P erturbation T heory
MG	Main G roup
TM	Transition M etal
RR	Reactant R egion
TSR	Transition S tate R egion
PR	Product R egion
NCI	Non-Covalent I nteraction

RDG	R educed D ensity G radient
US-EPA	U nited S tates E nvironment P rotection A gency
NHC	N - H eterocyclic C arbene
GGA	G eneralized G radient A pproximation
hGGA	h ybrid G eneralized G radient A pproximation
STQN	S ynchronous T ransit- G uided Q uasi- N ewton (Algorithm)
PCM	P olarizable C ontinuum M odel

Physical Constants

Speed of Light	c	$=$	$2.99792458 \times 10^8 \text{ m s}^{-1}$
Planck's Constant	h	$=$	$6.62607004 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$
Boltzmann's Constant	k_B	$=$	$1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$
Gas Constant	R	$=$	$8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$
Pi	π	$=$	3.1415926535

Symbols

ξ	intrinsic reaction coordinate	Bohr amu ^{1/2}
ξ^*	reduced reaction coordinate	unitless
E	energy	kcal mol ⁻¹
$F(\xi)$	reaction force	kcal mol ⁻¹ ξ ⁻¹
$W_i \quad i = 1, 2, \dots$	reaction work	kcal mol ⁻¹
$\Delta E^\ddagger$	activation energy	kcal mol ⁻¹
ΔE°	reaction energy	kcal mol ⁻¹
$\Delta G^\ddagger$	activation Gibbs free energy	kcal mol ⁻¹
ΔG°	reaction Gibbs free energy	kcal mol ⁻¹
N	number of electrons	unitless
M	number of atoms	unitless
$v(\mathbf{r})$	external potential	Hartree
μ	electronic chemical potential	kcal mol ⁻¹
χ	Mulliken's electronegativity	kcal mol ⁻¹
I_1	first ionization potential	kcal mol ⁻¹
A_1	first electron affinity	kcal mol ⁻¹
ϵ_H	HOMO energy	eV, kcal mol ⁻¹
ϵ_L	LUMO energy	eV, kcal mol ⁻¹
$J(\xi)$	reaction electronic flux	kcal mol ⁻¹ ξ ⁻¹
$f(\mathbf{r})$	Fukui function	a.u.
$\rho(\mathbf{r})$	electron density	a.u.
$f^+(\mathbf{r})$	electrophilic Fukui function	a.u.
$f^-(\mathbf{r})$	nucleophilic Fukui function	a.u.

$\phi_i(\mathbf{r})$ $i = 1, 2, \dots$	molecular orbital	unitless
η	molecular hardness	kcal mol ⁻¹
$f^{(2)}(\mathbf{r})$	dual descriptor	a.u.
λ_i $i = 1, 2, \dots$	density Hessian eigenvalues	a.u.
$\nabla^2\rho(\mathbf{r})$	electron density Hessian matrix	a.u.
Q	atomic charge	e
ΔQ_{A-B}	A–B bond polarity index	e

Dedicated to my beloved wife and my lovely princess...
Abigail and Amelia

"I can do all things through Christ who strengthens me."
Philippians 4:13

Chapter 1

General Introduction

Transition metals (TM) have dominated all branches of homogeneous and heterogeneous catalysis along the years. In particular, fine chemical transformations can be carried out by means of tuning the reactivity through changes of steric hindrance, metal center, solvent, among others factors. Some outstanding examples in TM catalysis encompass reactions such as metathesis [2–7], Heck [8–14], and Suzuki-Miyaura reactions [15–17], to cite a few examples. One of the major problems in homogeneous catalysis is the difficultness of recovering the catalyst from the reaction media along with its high cost and high toxicity of the TMs when they are compared with main group (MG) elements [18–21].

Table 1.1 summarizes the main differences between TM and MG elements. The most characteristic difference between TM and MG catalysts is that the former have partially occupied valence *d* orbitals that lie close in energy. Therefore, the small energy gap in TM compounds allows these systems a pronounced interaction with small molecules, such as CO, CO₂, and H₂. On the contrary, MG compounds show valence *s* or *p* orbitals that are either fully occupied or empty, but far apart energetically. Since an often huge energy gap is observed in MG compounds, poor interaction with small molecules is obtained. The relevance of the activation of small molecules is because it is a key step in most catalytic cycles.

Transition-metal compounds	Main-group compounds
Usually have partially occupied valence d orbitals that are often relatively close in energy.	The valence s or p orbitals are either fully occupied or empty and are far apart energetically.
Often coloured as a consequence of small orbital energy separations.	Usually colourless.
Often interact with small molecules such as CO, C ₂ H ₄ or H ₂ .	Generally do not interact strongly with CO, C ₂ H ₄ or H ₂ .
Often paramagnetic.	Usually diamagnetic.
Stereochemical electron pair character less pronounced.	Have stereochemically active electron pairs which form the basis of VSEPR theory.

TABLE 1.1: Differences between transition metals and main group elements.

Generally, MG elements belonging to groups 13 and 14 are often stabilized in its 3+ and 4+ oxidation states, respectively. However, low valent group 13 and 14 compounds are so reactive and tend to carry oligomerization and disproportionation reactions. These reactions can take place due to the weakness of these bonds in which the non-classical oxidation state main group elements are involved [? ? ?]. For example, aluminum is often stabilized in its 3+ oxidation state. Although there are some reports in which aluminum centers exhibit valence 2+, Al¹⁺ centers are not thermodynamically stable [22–26]. A clear example is the high availability of AlCl₃ in contrast to AlCl.

The reason why low valent MG compounds are hard to be found in nature is because of the poor kinetic stability, and high thermodynamic stability in its higher oxidation states. Therefore, efforts for isolating MG based catalysts have been a major task in the development of low valent MG catalysis. Due to the low thermodynamic stability, efforts are centered on the use of kinetic stabilization techniques. In Figure 1.1, a general scheme that exemplifies the thermodynamic and kinetic stabilization in low valent main group elements. If we consider a forward reaction coordinate that leads to oligomerization and disproportionation (ξ), the thermodynamic and kinetic control can easily be explained. We consider a simple EH₂

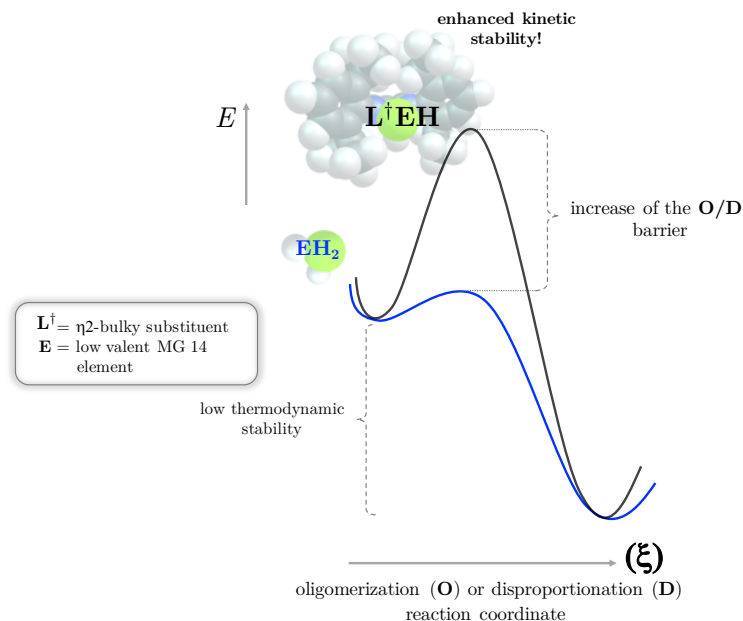


FIGURE 1.1: Energy profile for kinetic and thermodynamic stability in non-bulky and bulky low valent MG compounds.

and a bulky-ligand based compound $\text{L}^\dagger\text{EH}$. As can be seen, low thermodynamic stability is due because of the products of oligomerization and disproportionation are much more stable than the low-valent compounds. On the other hand, the engineering of bulky ligands help to increase the energy barrier toward undesired products and helping to gain kinetic stability.

Roesky *et al.* reported in 2000 the very first example of a stable monomeric aluminum(I) center bearing the diiminoacetylacetonate ligand NacNac (NacNac = $[\text{ArNC}(\text{Me})\text{CHC}(\text{Me})\text{NAr}]^-$ with $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) [27]. In this model, the bulky iPr groups avoid dimerization among the catalysts. Later in 2014, Nikonov and co-workers used the Roesky's compound to activate robust σ bonds (H-X : $\text{X} = \text{H}, \text{Si}, \text{B}, \text{Al}, \text{and C}$) through an oxidative addition mechanism ($\text{Al}^{1+} \rightarrow \text{Al}^{3+}$) [27–29]. The relevance of the activation of small molecules is because it is a key step in most catalytic cycles and this task has been – until a few time ago – an exclusive feature of TM catalysts.

In general, the high impact of using low valent main group complexes comes from the fact that they can react either through the lone pair of electrons on the metal center, in a carbene-like behavior [18, 20, 28, 30, 31] or as acidic centers by the presence of an empty p orbital. The behavior allows high effectiveness toward the activation of small molecules [18, 32, 33]. In this regard, MG elements have emerged as alternative compounds of the traditional TMs complexes [18, 19], becoming good candidates for a new branch of catalytic applications. Surprisingly, several complexes containing low valent MG elements react at room temperature without using any co-catalyst [32–34].

In this Thesis work, we study the application of low valent MG compounds toward the activation of small molecules. All the analyses that will be carried out in this Ph.D. thesis are aimed to gain a deeper understanding of low valent MG chemistry, motivate future experimental work, and to help explaining experimental data.

In Chapter 2, we study the activation and hydroboration of CO_2 toward the formation of formic acid derivatives using heavier group 14 NacNac catalysts (Si(II), Ge(II), Sn(II), and Pb(II)). Furthermore, in Chapter 3 the activation of H_2 using a NON-xanthene-based catalyst will be studied in great detail. Moreover, the substituent effect on simple alumanyl anions will be revealed through high-level coupled-cluster theory. The nature of the activation energies shall be studied using a distortion-interaction model and symmetry-adapted perturbation theory.

In this Thesis work, we also worked in advances for the computation of electronic activity along with a reaction through the reaction electronic flux (REF). Particularly, work was done to compute the REF when the Koopmans’ and finite difference approximation fails. This can be found in Appendix B

Chapter 2

Activation and Hydroboration of CO₂ by Low Valent Main Group Catalysts

2.1 Introduction

Massive CO₂ production has been linked to a profound atmospheric impact, whose origins are coming from natural and anthropogenic sources [35]. It is well-known that CO₂ is mostly responsible for the greenhouse gases, causing the “global warming”. In this regard, the “*United States Environment Protection Agency*” (US-EPA) reported that carbon dioxide is responsible for $\approx 82\%$ of the greenhouse gas emissions, with an equivalent to 6.673 million metric tons of CO₂ in atmosphere [36]. Although a little portion of CO₂ concentrations can be removed naturally by plants via the carbon cycle [37, 38], additional tools should be developed to reduce such concentrations through techniques that allow the control and transformation of the pollutant gases. This problem has caught the attention of specialists to make unflagging efforts to reduce the CO₂ concentrations from the atmosphere.

Nowadays, several chemical methods have been developed for the CO₂ transformation, but only a few of them have been industrially used [39, 40]. One of the most widely implemented method is the urea synthesis, which utilizes CO₂ in its main process [39–41]. Synthesis of poly and cyclic carbonates is another new industrialized process, which uses the reaction of CO₂ with epoxides in the presence of a catalyst [42, 43]. In a minor scale, CO₂ has also been used as feedstock for organic syntheses, such as carboxylations of C–H bonds [44, 45] and N–H bonds [45].

Some recent advances in CO₂ fixation have reported the use of N-heterocyclic carbenes (NHCs) to form imidazolium carboxylates [46, 47]. In this sense, improvements in reducing CO₂ have been achieved with transition metal (TMs) NHC complexes [48, 49]. Strategies mentioned above exhibit good results in fixation and activation of CO₂ under mild reaction conditions [50–53]. Moreover, it has been shown that a leading synthetic methodology in CO₂ fixation is easily accomplished by means of using TM through incorporation of this gas into complexes containing M–C bonds [54–58].

Roesky and co-workers have reported the CO₂ reduction by using stable low-valent Ge^(II) [32] and Sn^(II) [33] hydrides coordinated to N-Arylisopropyl- β -diketimate [also known as NacNac ligand (NacNac = [ArNC(Me)CHC(Me)NAr][−] with Ar = 2,6-*i*Pr₂C₆H₃)] (see complexes **2** and **3** in Scheme 2.1). On the other hand, efforts to obtain the low valent silicon(II) hydride derivative have been made but without success [59]. Unfortunately, the synthesis strategies for Ge and Sn analogs do not apply for silicon, most probably due to its high reactivity. The synthesis of **2** and **3** is carried out from the corresponding germanium(II) and tin(II) chlorides, NacNacGeCl and NacNacSnCl, respectively. The reaction is carried out by exchanging the chloride by the hydride through a Cl/H metathesis reaction. For Si^(II) the NacNacSiCl derivative is not accessible. Likewise, although lead β -diketimate halide [60, 61], aryloxide [62], amido [63], anilido [63] alcoxide [61, 64, 65], alkyl [66], phosphanide [64] complexes have been synthesized, no evidence for the hydride lead complex has been obtained to date. Moreover, CO₂ activation has been observed for tin and lead NacNac alcoxides, in which the dependence of the reaction rate and reversibility of the reaction is sensible upon minor changes in the alcoxide unit [65, 67].

The advantage of this kind of complexes is that they can react either through the lone pair of electrons on the metal center, in a carbene-like behaviour [18, 20, 28, 30, 31] and/or by a hydride transfer reaction [18, 32, 33]. In this regard, MG elements have emerged as alternative compounds of the traditional TMs complexes [18, 19], becoming good candidates for a new branch of catalytic applications. Surprisingly, several complexes containing low valent MG elements react at room temperature without using any co-catalyst [32–34].

Takagi and Sakaki [68] have performed a density functional theory (DFT) investigation in order to predict the catalytic cycle of **2** with (CH₃)₂CO, Ph₂CO and CF₃PhCO ketones, comparing the results with the (PPh₃)₂RhH organometallic catalyst. They found that ketones easily react with **2** to afford the corresponding Ge^(II) alkoxide. Also, a catalytic cycle for CO₂ activation was proposed, in which

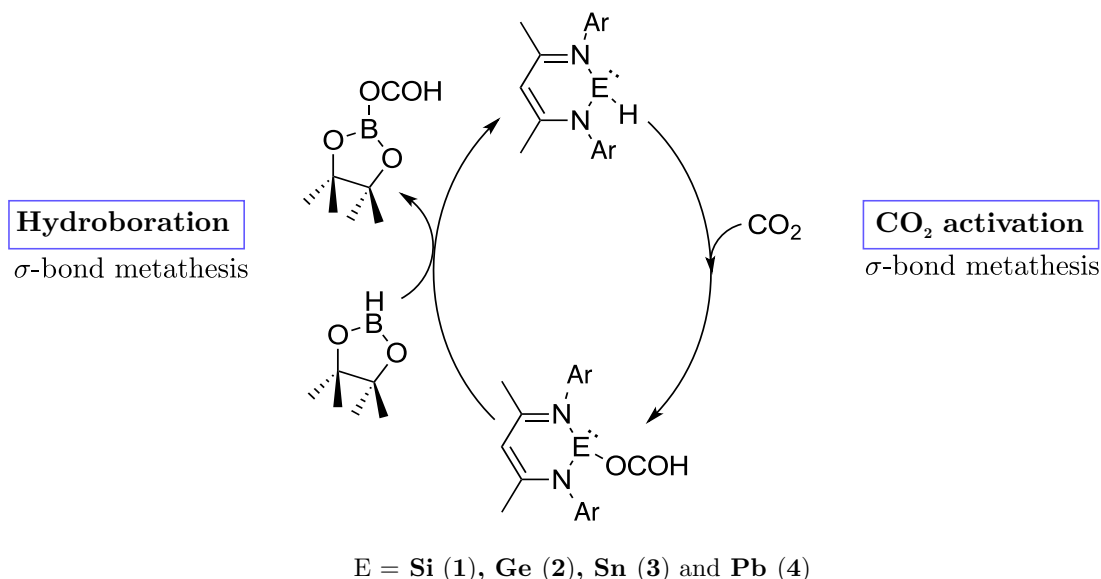


FIGURE 2.1: Catalytic cycle for the hydroboration/reduction of CO₂

SiF₃H was used as a hydride-source to restore the catalyst. However, to the best of our knowledge, no further theoretical studies for CO₂ activation using **2** have been reported; and no exploration using heavier group 14 elements have neither been attempted. Moreover, further analyses are necessary for a deeper understanding of the catalytic activity and applicability of MG based complexes in chemical reactions.

In this research, with the goal of proposing a catalytic cycle for the transformation of CO₂, HBpin has been selected as a hydride source to restore the MG catalyst. The proposed catalytic cycle is depicted in Figure 2.1. As can be seen, the reaction mechanism is governed by two main steps: the CO₂ activation and hydroboration steps. It is worth to mention that both steps correspond to σ -bond metathesis reactions. Hydroboration of CO₂ has shown to be an attractive process for the reduction of this gas. A clear example is a work by Jones *et al.* in which a TOF of 13,300 h⁻¹ was obtained for hydroboration of unactivated ketones using Ge^(II) and Sn^(II) catalysts [21]. It is worth to mention that besides the work of Sakaki [68], to the best of our knowledge comparisons of different hydride sources have

not been published to date.

In this chapter, the usage of MG catalysts (**1–4**) in the activation of CO₂ as well as hydroboration was explored employing quantum chemistry calculations. A full analysis of the reaction products was carried out with the aim of explaining accessible conformational isomers that can be formed after activation. The full catalytic cycle is studied using HBpin as a hydride source to restore the catalyst. All the analyses serve as proof that system **4** would perform better than the already synthesized complexes **2** and **3**.

2.2 Computational Details

Calculations were carried out at the DFT level using the hybrid meta-GGA M06-2X functional [69]. This method was selected because it is highly recommended for main group computations in order to obtain accuracy in both kinetic and thermochemistry as well as to correctly describe noncovalent interactions [69–71]. Si, Ge, Sn, and Pb were treated with the LANL2DZ basis sets and quasi-relativistic effective core potentials [72]. Second-row atoms were treated with the 6-31G(d, p) basis set [73, 74]. For comparison purposes, the activation of CO₂ was computed using the larger 6-311+G(d, p) basis set for the atoms mentioned above by performing single point calculations on the optimized structures obtained with the 6-31G(d, p) basis. Stationary points and transition states (TS) were verified by frequency calculations using analytic second derivatives [75]. The Berni Synchronous Transit-Guided Quasi-Newton (STQN) algorithm was used for searching the TS geometries [76, 77]. TS structures were connected with reactants and products using the intrinsic reaction coordinate methodology (IRC) [78–80] in mass-weighted cartesian coordinates, using a step size of 0.100 Bohr amu^{1/2}. To take into account solvent effects (toluene with a dielectric constant of 2.3741), single point computations were carried out on the optimized gas-phase geometries via the Polarizable Continuum Model (PCM) [81]. The reason for doing so is because optimization of the TS structures using PCM encountered serious convergence problems when Sn and Pb were treated. All computations were done in the Gaussian 09 software package [82]. The Multiwfn analyzer [83] was employed for wave function analyses. Bonding and charge analyses were carried out through the NBO [84] program interfaced with the Gaussian software.

Due to significant errors are obtained when the harmonic approximation is used to compute thermochemical quantities for low-frequency modes, the quasi-rigid rotor harmonic oscillator (quasi-RRHO) method was employed (see Appendix C). The vibrational entropy was computed by interpolating the rotational and vibration entropy since the latter goes to infinity while the frequency approaches zero.

This approach has been introduced by Grimme [85] and the reader is referred to Appendix C for a full explanation of the method and discussion regarding the parameters used to compute well-defined free energies. After the free energy correction is obtained, activation and reaction Gibbs free energies are computed as follows:

$$\Delta G = \Delta E + \Delta G_{RRHO}^T + \Delta \delta G_{solv}^T(X) \quad (2.1)$$

where ΔE corresponds to the gas phase electronic energy difference, ΔG_{RRHO}^T collects the Gibbs free energy correction with zero-point vibrational energies, and $\Delta \delta G_{solv}^T(X)$ accounts for solvation energy.

In order to qualitative characterize noncovalent interactions, the NCIPLOT program was used. However, for quantitative analyses of noncovalent interactions of relevant structures, symmetry-adapted perturbation theory (SAPT) [86] has been used. The reader is referred to Appendix 2.7 for a brief explanation of SAPT. All SAPT computations were carried out in Psi4 [87]. Specifically, DF-SAPT0 [88, 88, 89] was used in all computations with the cc-pVDZ basis set.

2.3 Results and Discussion

2.3.1 Starting the Catalytic Cycle: The CO₂ Activation Step

The CO₂ activation mechanism is classified as a σ -bond metathesis reaction. The CO₂ activation step is shown in Figure B.9. In the first stage, long-range interactions between CO₂ and the catalyst allow the formation of the reactant complex (**R**). Afterwards orbital interactions will rule the second step, *i.e.*, the activation of CO₂ by the MG-complex. There are two ways in which CO₂ can approach the catalyst, giving rise to different TS structures and therefore different stereoisomers are formed. The first reaction path is obtained when CO₂ frontally approaches the **E**–H bond, labeled as the front-side approach. The second reaction path arises from the backward approach of CO₂, this pathway corresponds to the back-side approach. In Figure 2.3, the front-side and back-side approaches are labeled as **R1** and **R2**, respectively. Albeit the reaction mechanism does not change significantly in both pathways, different conformational stereoisomers are obtained as final products. It is worth noting in Figure 2.3 that hydride complexes exhibit an *endo* conformation where the metal center and the hydride are below the NCCCN plane and the **E**–H bond is roughly perpendicular to the same plane. The latter is in agreement with related alkoxide complexes with non-bulky alkyl substituents. On the contrary, it has been observed that bulky ligands force the complex to adopt an *exo* conformation [66, 90].

For the isolated CO₂ molecule, the carbon atom behaves as an electron deficient center with an electronic charge (Q) of $+1.06|e|$, while the charge per oxygen atom is $-0.53|e|$. In complexes **1-4**, the hydrogen atom bonded to the metal center behaves as an hydride, it appears negatively charged: $-0.29|e|$ (**1**), $-0.32|e|$ (**2**), $-0.40|e|$ (**3**), and $-0.41|e|$ (**4**). The increase of electron population on the hydride atom correlates well with the respective charge depletion for the metal center,

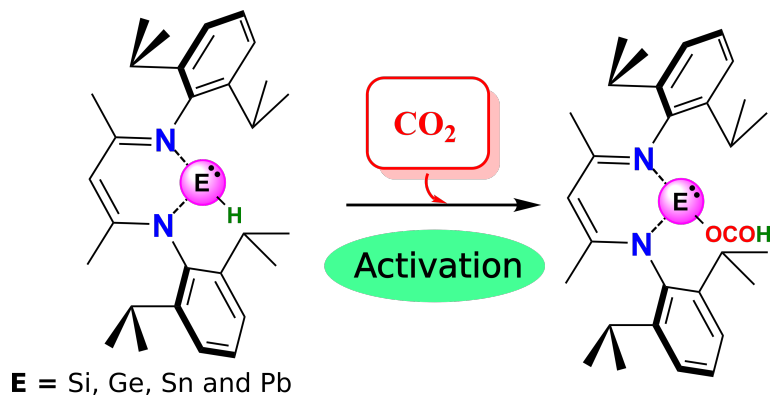


FIGURE 2.2: CO_2 activation by the main group $\text{Si}^{\text{(II)}}$ (**1**), $\text{Ge}^{\text{(II)}}$ (**2**), $\text{Sn}^{\text{(II)}}$ (**3**) and $\text{Pb}^{\text{(II)}}$ (**4**) based catalyst. CO_2 insertion in the $\mathbf{E}\text{--H}$ bond is schematized in color-code.

$+0.75|e|$ (Si), $+0.83|e|$ (Ge), $+1.00|e|$ (Sn), and $+1.02|e|$ (Pb). An important result arises here, which will serve as a proof to establish the reactivity trend in group 14 NacNac catalysts. The difference between the metal atomic charge and that on the hydride atom ($\Delta Q_{\mathbf{E}\text{--H}} = |Q_{\mathbf{E}} - Q_{\text{H}}|$), serve as indicator of the polarity of the $\mathbf{E}\text{--H}$ bond. The heavier the MG element, the larger $\mathbf{E}\text{--H}$ bond polarity is obtained. The values obtained for $\Delta Q_{\mathbf{E}\text{--H}}$ were found to be $1.04|e|$, $1.15|e|$, $+1.40|e|$ and $+1.43|e|$ for complexes **1**, **2**, **3**, and **4**, respectively. These values will be discussed later in the text in more detail, see Section 2.3.1.2. Since the reaction mechanism is ruled by a σ –bond metathesis at first, two electrostatic interactions would drive the CO_2 approach to the $\mathbf{E}\text{--H}$ fragment, these are the $\text{C}\cdots\text{H}$ and $\text{O}\cdots\mathbf{E}$ interactions. The molecular electrostatic potential depicted in Figure 2.4 characterizes these specific interactions. Additionally, the $\text{H}\cdots\text{O}$ and $\mathbf{E}\cdots\text{C}$ interactions are electrostatically destabilizing and consequently the $\mathbf{E}\text{--COOH}$ product is not allowed.

Frontier molecular orbitals were examined to rationalize the orbital-controlled interaction between the reactants. Figure 2.5 depicts the densities for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for CO_2 and complexes **1**–**4**. In Figure 2.6 the main contributions to the HOMO orbital are presented ($\mathbf{E}$ = group 14 element, H = hydride and L =

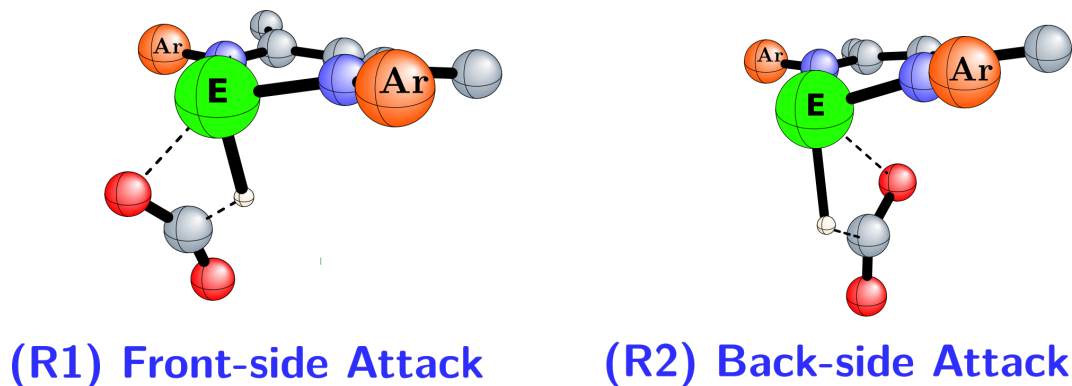


FIGURE 2.3: Approaches of CO_2 to the **1-4** MG-complexes. For the sake of clarity hydrogen atoms attached to carbons and $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ are omitted from the molecular representations. Oxygens are in red, nitrogens are in blue, carbons are in grey, and hydride is colored in white.

Ligand). As observed in Figure 2.5, the HOMO is localized on the metal center and the hydride atom, with contributions of 76% (**1**), 58% (**2**), 56% (**3**) and 10% (**4**) from the metal and up to 21% from the $1s$ orbital of the hydride (Figure 2.6). These results indicate that when CO_2 is close enough to the E-H bond, the $1s$ orbital of H interacts with the LUMO orbital of CO_2 , which is mainly centered on the carbon atom (62%) with $2p_y$ and $3p_y$ atomic orbitals contributing the most.

The low contribution of the Pb atom to the HOMO orbital in complex **1** prompted us to perform relativistic calculations to evaluate whether this effect plays a significant role or not. Results summarizing differences in molecular orbital isosurfaces by the inclusion of relativistic effect are summarized in Appendix D.2.2. It was found that the effect of relativism is not significative regarding energy differences (Appendix D.2.1) but on reactivity. Therefore, the disappearance of the HOMO orbital over the Pb atom is mainly due to the lack of relativistic effects as evaluated by using the Douglas-Kroll-Hess (DKH) Hamiltonian. See Appendix D.2.2 for a more detailed discussion.

In addition, the dual descriptor [91, 92] was computed to characterize the reactivity of the systems **1-4**, which allows to rationalize the reactivity in terms of the simultaneous knowledge of nucleophilic and electrophilic sites within a molecule

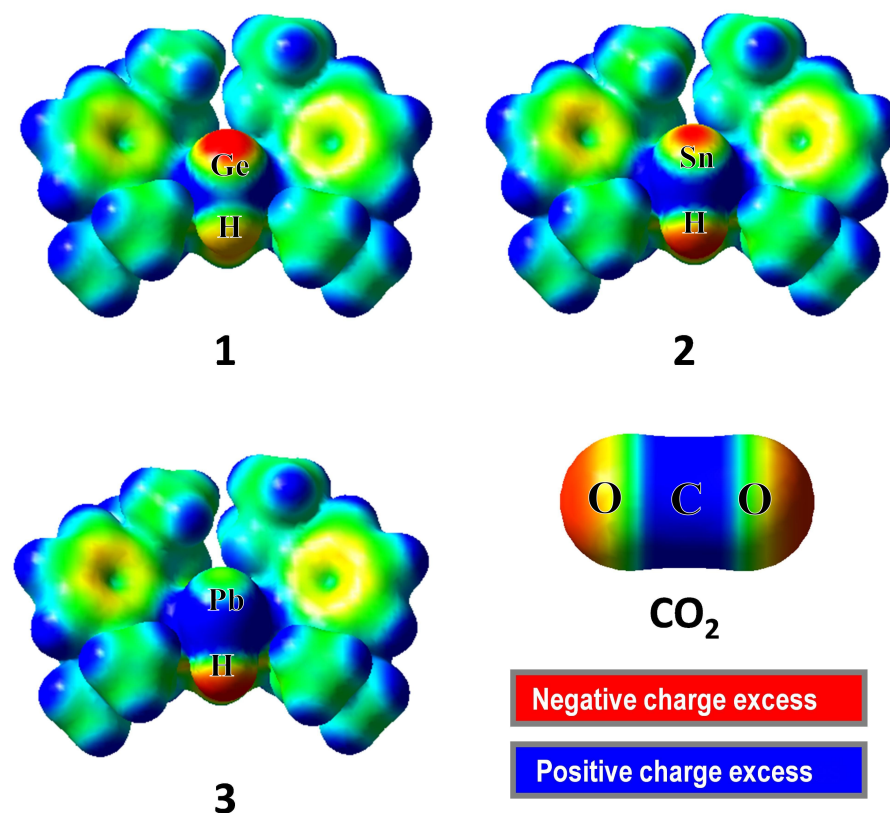


FIGURE 2.4: Molecular electrostatic potential of complexes **1-4** and CO_2 .

[93–98]. Dual descriptor of complexes **1-4** and CO_2 are shown in Figure 2.5. Nucleophilic and electrophilic sites are represented in red and green, respectively. The hydride atom is characterized as a high nucleophilic site, while the nucleophilic character of the metal center progressively dissipates. The reaction is initiated by the nucleophilic attack of the hydride to the carbon atom of CO_2 . Once the reactant complex is formed, the reaction mechanism involves the following main chemical events: (i) breaking of the $\sigma\text{E-H}$ bond and (ii) formation of a C–H bond; coordination of CO_2 takes place through formation of a E-O bond. All these chemical events take place in a single step but with different degrees of synchronicity.

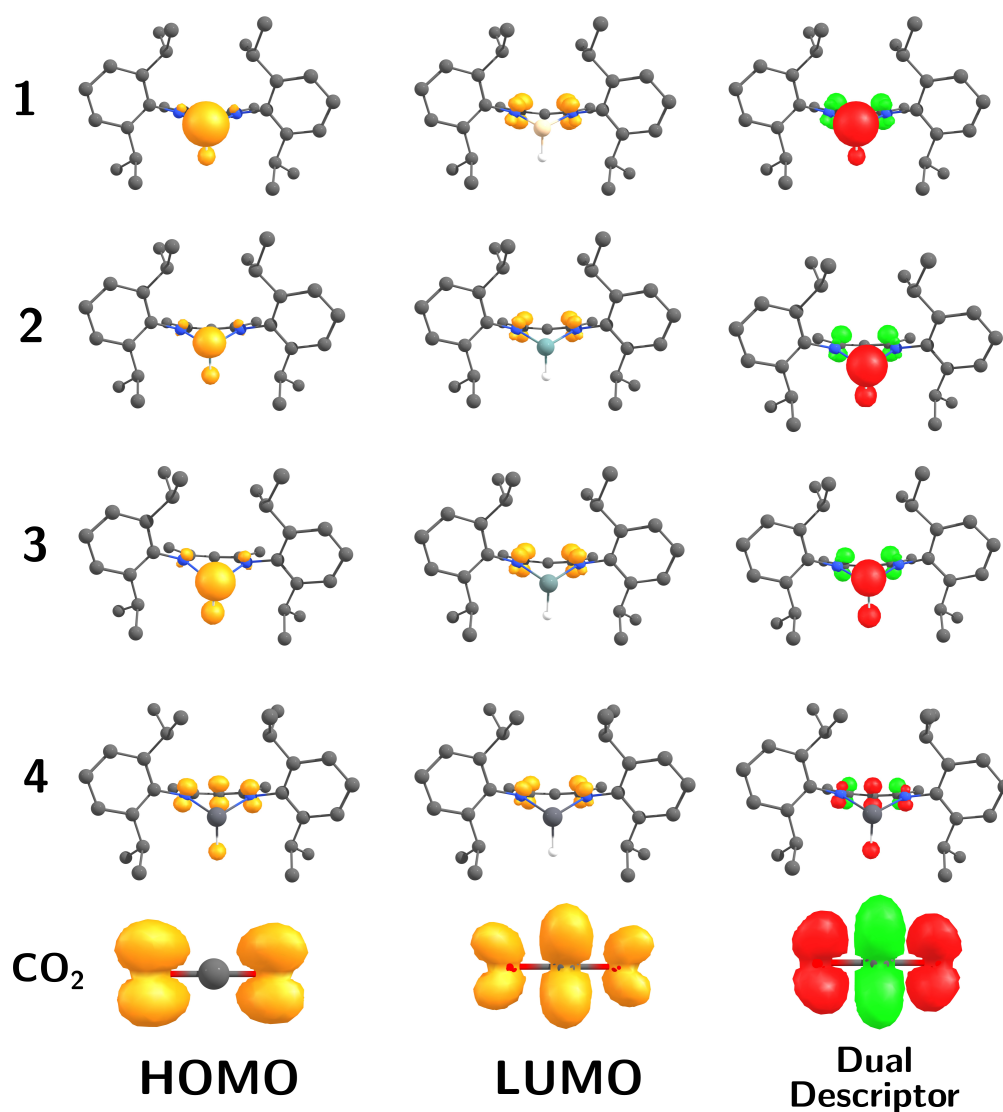


FIGURE 2.5: HOMO-LUMO densities and dual descriptor computed for complexes 1-4 and CO_2 molecule (isovalue 0.01 a.u.). For dual descriptor, nucleophilic and electrophilic zones are represented in red and green, respectively. Hydrogen atoms attached to carbons were omitted for clarity.

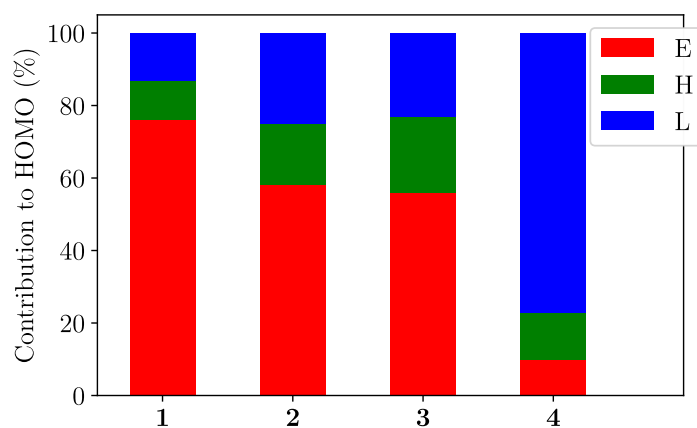


FIGURE 2.6: Contribution from main group element (**E**), hydride (**H**) and NacNac ligand (**L**) to the HOMO orbital.

2.3.1.1 The Reactant Complex

As noted above, the reaction mechanism starts with electrostatic interactions between CO₂ and the MG-complex, giving rise to a pre-reactive complex **R**. For all the systems, the distance between the hydride and the carbon atom of CO₂ (**E**–H···CO₂) is ~ 2.5 Å, with weak interaction energies ranging from -4.0 to 0.4 kcal mol⁻¹ (Table 2.1). To analyze in great detail the noncovalent interactions of CO₂ with complexes, symmetry-adapted perturbation theory (SAPT) calculations were performed for catalyst **2** as representative. SAPT allows partitioning the interaction energy in terms of electrostatic, exchange, induction and dispersion contributions. Results from SAPT0 calculations for (**2** + CO₂)@**R1** are shown in Figure 2.7¹. As can be seen from Figure 2.7, both electrostatic and dispersion interactions rule the formation of the reactant complex, with a minor contribution coming from induction interactions due to the large separation of the fragments. From the latter, induction energy seems to be dominated by polarization instead of charge transfer². Finally, total SAPT interaction energies for **R1** and **R2** paths were found to be -1.4 and -1.6 kcal mol⁻¹, respectively, differing a bit from the ones obtained in Table 2.1 that could be contaminated with basis set superposition error.

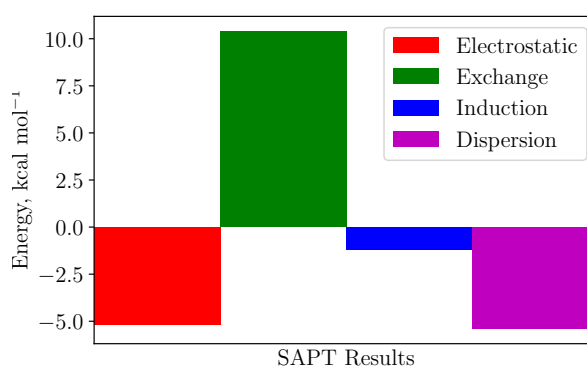


FIGURE 2.7: SAPT0 results for the reactant complex in the (**2** + CO₂)@**R1** reaction pathway.

¹Quite similar numerical results were found for the back-side approach.

²Charge transfer energies computed using SAPT through the procedure described by Misquitta and Stones are less than -0.4 kcal mol⁻¹

2.3.1.2 CO_2 Activation

Once the reactive complex **R** is formed, structural and electronic rearrangements start to take place, driving the reduction mechanism of CO_2 . We have computed SAPT0 for each structure from the reactant complex to the TS through the minimum energy path. Results are shown in Figure 2.8. From Figure 2.8 it can be seen that while the σ -bond metathesis mechanism takes place, the dispersion component remains steady compared to a sharp stabilization of the reacting species driven by electrostatic interactions at the TS vicinity. Accordingly, the induction (polarization + charge transfer) term, which is close to zero at the reactant complex, becomes the most favorable interaction at the TS structure.

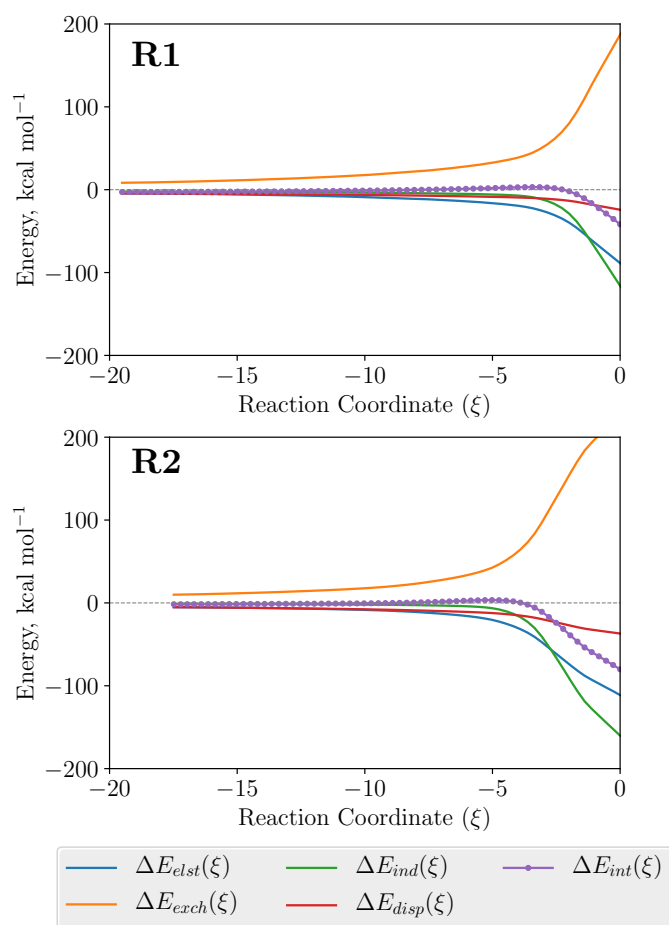


FIGURE 2.8: SAPT0 along the reaction coordinate for $(\mathbf{2} + \text{CO}_2)@\mathbf{R1}$ and $(\mathbf{2} + \text{CO}_2)@\mathbf{R2}$ reaction pathway.

Reaction	E_R	$\Delta E^\ddagger$	$\Delta G^\ddagger$	$\Delta E_r^\ddagger$	ΔE°	ΔG°	k (s ⁻¹)
(1 + CO ₂)@ R1	1.3	22.0 (20.8)	21.6	41.9	-19.9 (-17.5)	-16.6	9.1×10^{-4}
(1 + CO ₂)@ R2	-2.7	17.2 (18.0)	18.5	39.4	-22.2 (-20.0)	-17.8	1.7×10^{-1}
(2 + CO ₂)@ R1	0.4	14.8 (14.0)	15.9	35.7	-20.9 (-19.8)	-17.5	1.4×10^1
(2 + CO ₂)@ R2	-2.9	13.2 (10.8)	14.9	34.8	-21.6 (-21.0)	-17.5	7.4×10^1
(3 + CO ₂)@ R1	-3.5	8.6 (6.7)	7.4	33.5	-24.9 (-25.0)	-22.3	2.3×10^7
(3 + CO ₂)@ R2	-4.0	8.7 (6.3)	9.5	33.4	-24.7 (-25.1)	-21.0	6.8×10^5
(4 + CO ₂)@ R1	-3.3	3.7 (2.1)	4.8	29.0	-25.3 (-25.7)	-21.2	1.9×10^9
(4 + CO ₂)@ R2	-3.2	4.4 (2.2)	4.0	28.4	-24.0 (-24.7)	-20.3	7.3×10^9

TABLE 2.1: Interaction energy of fragments at the reactant complex ($E_R = E_{(C\ CO_2)R} - (E_C + E_{CO_2})$), activation ($\Delta E^\ddagger = E_{(C\ CO_2)TS} - (E_C + E_{CO_2})$), reverse activation ($\Delta E_r^\ddagger = E_{(C\ CO_2)TS} - E_{(C\ CO_2)P}$) and reaction energy ($\Delta E^\circ = E_{(C\ CO_2)P} - (E_C + E_{CO_2})$); $E_{(C\ CO_2)R}$, $E_{(C\ CO_2)TS}$ and $E_{(C\ CO_2)P}$ correspond to the energy of the complex-CO₂ system in the reactant complex, transition state and product, respectively. E_C and E_{CO_2} are energies of the isolated complex and CO₂, respectively. $\Delta E^\ddagger$ and ΔE° energies computed using the 6-311+G(d,p) basis set are shown in parenthesis. All electronic energies are referenced to isolated reactants, given in kcal mol⁻¹ and corrected with zero point energies in toluene.

It is worth to mention that reactions take place by bubbling dry CO₂ gas in presence of complex **2** or **3** in toluene (at ambient conditions) to afford the corresponding Ge^(II) or Sn^(II) formates, respectively [32, 33]. To take into account solvent effects, we calculated electronic and free energies in toluene at 298.15 K using the polarizable continuum model (PCM). Transition state structures together with selected geometrical parameters are shown in Figure B.4 for the eight reactions under consideration. In all cases, the TS structure exhibit a four-membered ring delimited by the interaction between CO₂ and the **E**-H bond is formed. The first mechanistic event is the $\sigma(\text{E-H})$ bond breaking that induces the hydride transfer to the carbon atom of CO₂. The second event taking place in parallel is the nucleophilic attack of the oxygen (O1) atom on the metal core. At this point, the C-H and **E**-O1 distances become shorter and longer, respectively, going from the front- to the back-side mechanism, while going from Ge^(II) to Pb^(II) both distances become longer. This behavior is a direct consequence of the increase in atomic radii.

Activation and reaction energies, together with estimated rate constants are quoted

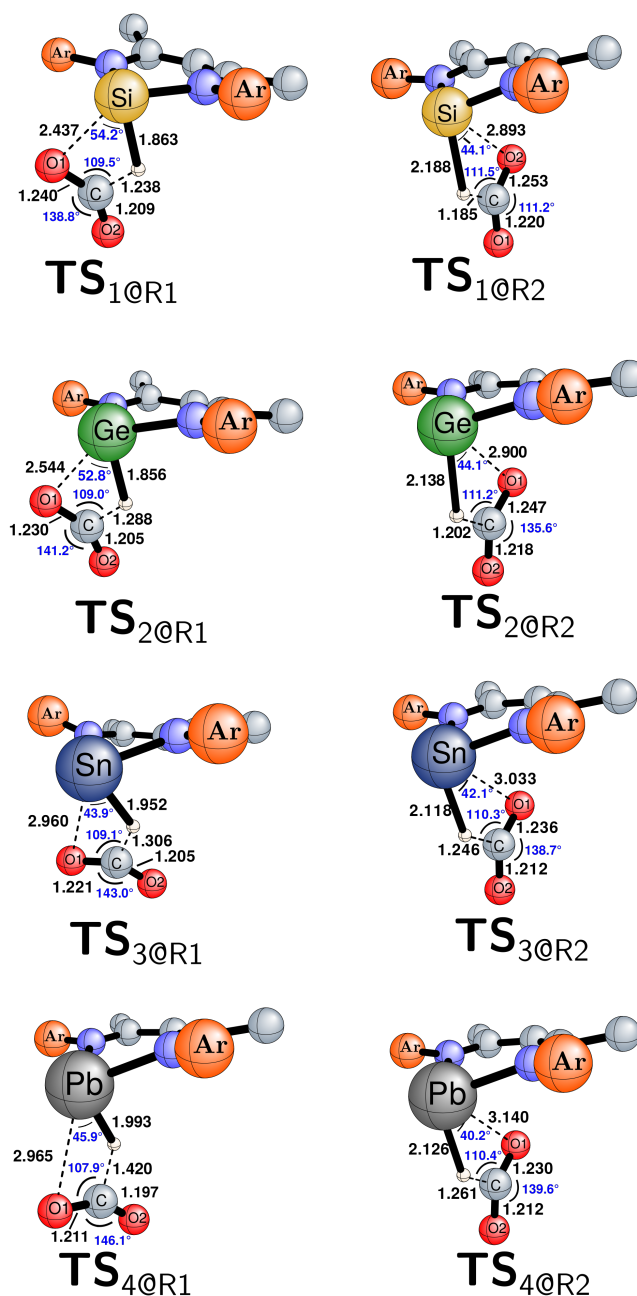


FIGURE 2.9: Transition state structures for both front- and back-side approaches (**R1** and **R2**), respectively. Hydrogens attached to carbons and $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ are omitted from the molecular representations. Bond distances and angles are in (Å) and degrees (°), respectively.

in Table 2.1. Gibbs free energies ($\Delta G^\ddagger$) were computed as mentioned in the Computational Details and Appendix C. Rate constants (k) were computed following transition state theory at standard ambient temperature (298.15 K), assuming a

first order (unimolecular) reaction. Activation energies (activation Gibbs free energies) for the front-side reaction monotonically decreases when going from Si to Pb with values of 22.0 (21.6), 14.8 (15.9), 8.6 (7.4) and 3.7 (4.8) kcal mol⁻¹, respectively. For the back-side pathway these energies were found to be 17.2 (18.5), 13.2 (14.9), 8.7 (9.5) and 4.4 (4.0) kcal mol⁻¹, respectively. From the results, it is expected that activation energies are low enough to activate CO₂ at room temperature and mild reaction conditions. This result validates our computational methodology, and it is in agreement with recent experimental observations, where the CO₂ activation proceeds even without using a co-catalyst [18, 32, 33]. Notice that the difference between the activation free energies of both approaches ($\Delta\Delta G^\ddagger = \Delta G_{\mathbf{R1}}^\ddagger - \Delta G_{\mathbf{R2}}^\ddagger$) are 3.1, 1.0, -2.1 and 0.8 kcal mol⁻¹ for complex **1**, **2**, **3**, and **4**, respectively. For Ge and Pb-based catalysts, this difference is close to the chemical accuracy limit of 1 kcal mol⁻¹ and therefore both activation pathways are quite competitive at ambient conditions. Regarding complex **1** the back-side approach is preferred by 3.1 kcal mol⁻¹, in contrast with catalyst **3** where the front-side approach is kinetically preferred since it is favored by 2.1 kcal mol⁻¹ over **R2**.

For comparison purposes, $\Delta E^\ddagger$ and ΔE° were computed in toluene with the larger 6-311+G(d, p) basis set at the M06-2X/6-31G(d, p) gas phase geometries. These values are reported within parenthesis in Table 2.1. As can be seen, although the activation barrier becomes lower with the increase of the basis set and inclusion of diffuse functions (with the most significant difference of 2.5 kcal mol⁻¹), the energies follow a similar trend of those obtained with the 6-31G(d, p) basis set. The same can be concluded with reaction energies when both basis sets are compared. Given the comparison and numerical results obtained, energetics with the 6-31G(d, p) basis are reported hereafter.

As for Pb, there are no reports of the synthesis of a stable NacNacSiH compound. Some reports of silicon(II) monohydride include stabilizing external agents as Lewis acids or TMs that can interact with the silylene lone-pair [59, 99]. Although several Si-based examples have been prepared, its use in CO₂ activation

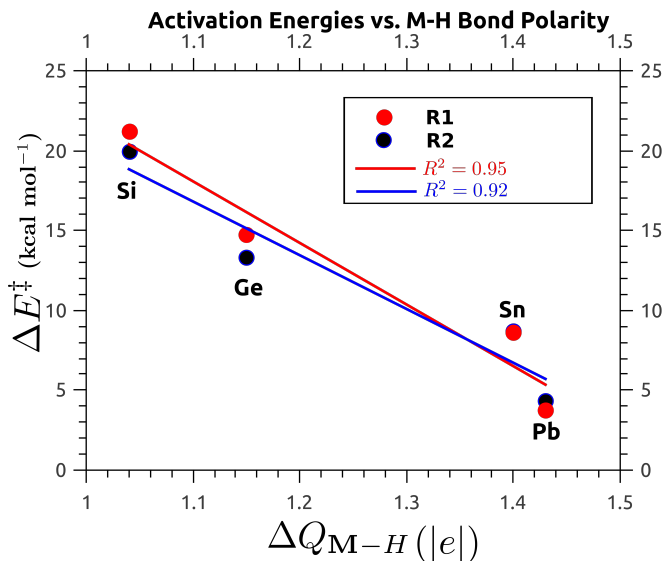


FIGURE 2.10: Linear relationship between activation energies ($\Delta E^\ddagger$) and bond polarity index ($\Delta Q_{\mathbf{E}-H}$) for complexes studied including silicon for the **R1** and **R2** pathways (**R1**, $\Delta E^\ddagger = -38.6\Delta Q_{\mathbf{E}-H} + 60.5$; **R2**, $\Delta E^\ddagger = -33.7\Delta Q_{\mathbf{E}-H} + 53.8$)

is unknown [100]. For the sake of completeness, we have computed the activation of CO₂ by using the NacNacSiH derivative. Activation energies of 22.0 and 17.2 kcal mol⁻¹ were found for the **R1** and **R2** pathways, respectively. Moreover, the computed reaction energies (-19.9 and -22.2 kcal mol⁻¹ for **R1** and **R2**) are quite similar to those obtained for complexes **2**, **3** and **4**. From these results, the silicon-based catalyst is found to be the least reactive toward the transformation of CO₂ compared with the heavier congeners of the group. On the other hand, given the low energy barriers and relative large exothermicities obtained for reactions (**4** + CO₂)@**R1** and (**4** + CO₂)@**R2**, it can be concluded that the CO₂ activation mediated by the Pb^(II) hydride complex would be both thermodynamically and kinetically viable under mild reaction conditions, thus it would perform the best for CO₂ capture. Moreover, due to the large values of reverse activation energies, the CO₂ releasing process seems to be less probable for the series studied.

Activation energies displayed in Table 1 enable us to establish a trend in reactivity of these low valent group 14 hydrides toward CO₂ activation. It is worth noting that the reactivity of the catalysts increases as the atomic radii of the MG element

increases. The reason of this behavior is because the Lewis acid character of the metal center increases when going down in group 14, which generates a more polar $\mathbf{E}^{\delta+}\text{--H}^{\delta-}$ bond that progressively promotes the hydride transfer reaction. This is confirmed by the bond polarity index (BPI; $\Delta Q_{\mathbf{E-H}}$) introduced previously. BPI values are $1.04|e|$ (Si–H), $1.15|e|$ (Ge–H), $1.40|e|$ (Sn–H) and $1.43|e|$ (Pb–H). These results indicate that Sn and Pb complexes are expected to be more reactive toward CO₂ than the Si and Ge analogs. In Figure 2.10 activation energies are plotted against the BPI for each reaction. Figure 2.10 gives a clear view of the linear dependence of activation energies with the polarity of the $\mathbf{E}\text{--H}$ bond. It is interesting to note from the linear dependence of $\Delta E^\ddagger$ with the BPI that a barrierless reaction would be obtained if the index reaches roughly $1.60|e|$. This task could be achieved tuning the polarity of the $\mathbf{E}\text{--H}$ employing electron-withdrawing groups at the vicinity of the $\mathbf{E}\text{--H}$ bond or by changing the polarity of the solvent. On the other hand, the same result shows that a future metallic behavior of C^(II) seems difficult to be achieved since high energy barriers would prevent it. In summary, we have provided evidence that the charge separation in the $\mathbf{E}\text{--H}$ bond seems to be responsible for the observed reactivity trend of these catalysts toward CO₂, ordered as $\text{Pb}^{(\text{II})} > \text{Sn}^{(\text{II})}$ [33] $>$ $\text{Ge}^{(\text{II})}$ [32] $>$ $\text{Si}^{(\text{II})}$.

Experimentally, addition of CO₂ to **2** in toluene initiates the reaction. The solution *slowly* changes color from red to yellow, giving place to the germanium formate [32]. However, the reaction using **3** *instantaneously* changes the color from yellow to colorless. The observed rates of these reactions are consistent with the computational estimated rate constants quoted in Table 2.1. As can be seen, reactions with **3** are several orders of magnitude faster than when complex **2** is used. As readily seen in Table 2.1, CO₂ activation with Pb^(II) hydride complex is the fastest reaction in both pathways. A similar trend has been found by activation and subsequent hydroboration (using HBpin, pin = pinacolato) of bulky and unactivated carbonyl compounds employing a low valent Ge^(II) and Sn^(II) catalyst [21]. It was found that hydroboration after activation of ketones is the rate-determining step, being the tin catalyzed reactions faster than those carried out using germanium.

This fact was attributed to the polarity of the **E**-O bond that increases as the metal size increases along the group.

2.3.1.3 Conformational Analysis

For both reaction paths, **R1** and **R2**, the CO₂ activation leads to the corresponding metal formates **P_{EH*i*}** and **P_{EH*o*}** (Figure 2.11). The notation comes from the spatial orientation of the hydride with respect to the NacNac ligand: pointing inside (*Hi*) or outside (*Ho*) the ligand. It was previously established that for complexes **2**, **3** and **4** both reaction mechanisms are competitive ($|\Delta\Delta G^\ddagger| < 2.1$ kcal mol⁻¹) and thus both products (**P_{EH*i*}** and **P_{EH*o*}**) are kinetically favored and equally expected to be formed (Table 2.1). Moreover, from the product stabilities plotted in Figure 2.12 (energies computed in toluene with ZPE correction), for Ge and Sn the energy differences between both possible products **P_{EH*i*}** and **P_{EH*o*}** are also quite small (0.7 and 0.2 kcal mol⁻¹ for Ge and Sn, respectively). These reactions can be classified as isoenergetics due to the thermal energy $k_B T$ is just 0.6 kcal mol⁻¹ at 298 K (k_B stands for the Boltzmann constant).

The crystallographic structure reported for the reaction of **2** with CO₂ corresponds to the **P_{2H*o*}** [32], which comes from the **R2** pathway. Although it is well known that most of the crystal structures differ from the lowest energy conformations [101], the existence of **P_{2H*o*}** agrees well with our computations: **P_{2H*o*}** is just slightly stabilized compared to **P_{1H*i*}** in 0.7 kcal mol⁻¹. The later result proposes a mixture composed by a 77% **P_{2H*o*}** and 23% **P_{2H*i*}** will coexist in toluene solution at ambient temperature, in accordance with a standard Boltzmann distribution. It is worth to mention that taking into account rather low barriers of conformational interconversions for the **P₂** isomers (Figure 2.12), it should be expected that the mixture be also composed by **P_{2O*o*}** and **P_{2O*i*}**.

Takagi and Sakaki have reported **P_{2H*o*}** as the only product obtained from both approaches, in apparent contradiction with our findings [68]. This result prompted us to perform a conformational study with the aim of connecting both isomers. In this context, rotation of the **E–O** bond was studied. It has been found that **R1** and **R2** cannot be connected through simple rotation of the **E–O** bond since the

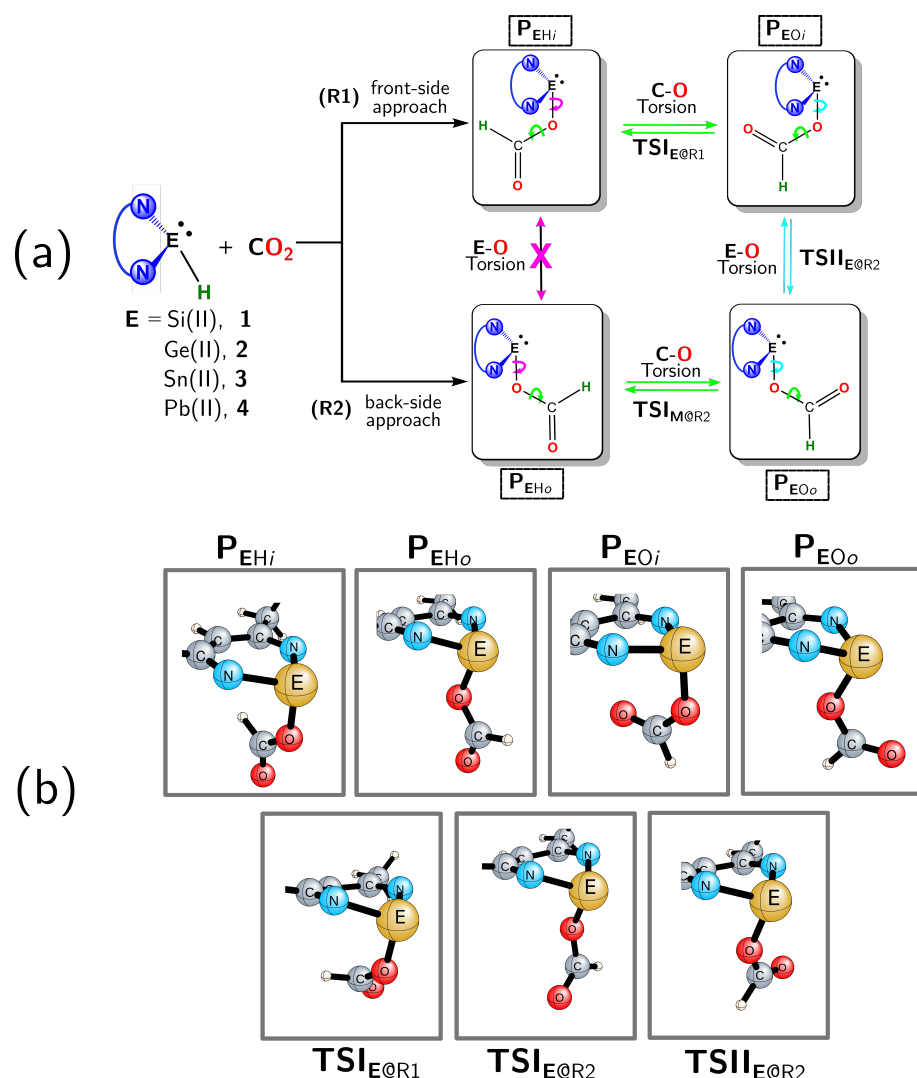


FIGURE 2.11: Representation of the conformational stereoisomers obtained as products of the reactions between complexes **1-4** and CO₂. The products from both approaches (**R1** and **R2**) are named **P_{EH_i}** and **P_{EH_o}**, respectively. The free torsion around the C–O bond (green arrow) afford the more stable complexes **P_{EO_i}** and **P_{EO_o}**, respectively. Other possible interconversions are also shown by rotating the M–O bond (magenta and turquoise arrows). E–O torsion in magenta was found to be not possible. The bidentated NacNac ligand was schematized by connected nitrogen atoms (blue).

steric hindrance presented by the bulky aryl groups (2,6-*i*Pr₂C₆H₃) at the NacNac ligand prevents the straightforward interconversion between **P_{2H_i}** and **P_{2H_o}**. Instead, a new set of conformers was found: **P_{EO_i}** and **P_{EO_o}** (labelled in accordance with spatial orientation of the carbonyl oxygen with respect to the NacNac ligand). These rotamers arise from the restricted rotation of the C–O bond and are also quoted in Figure 2.11.

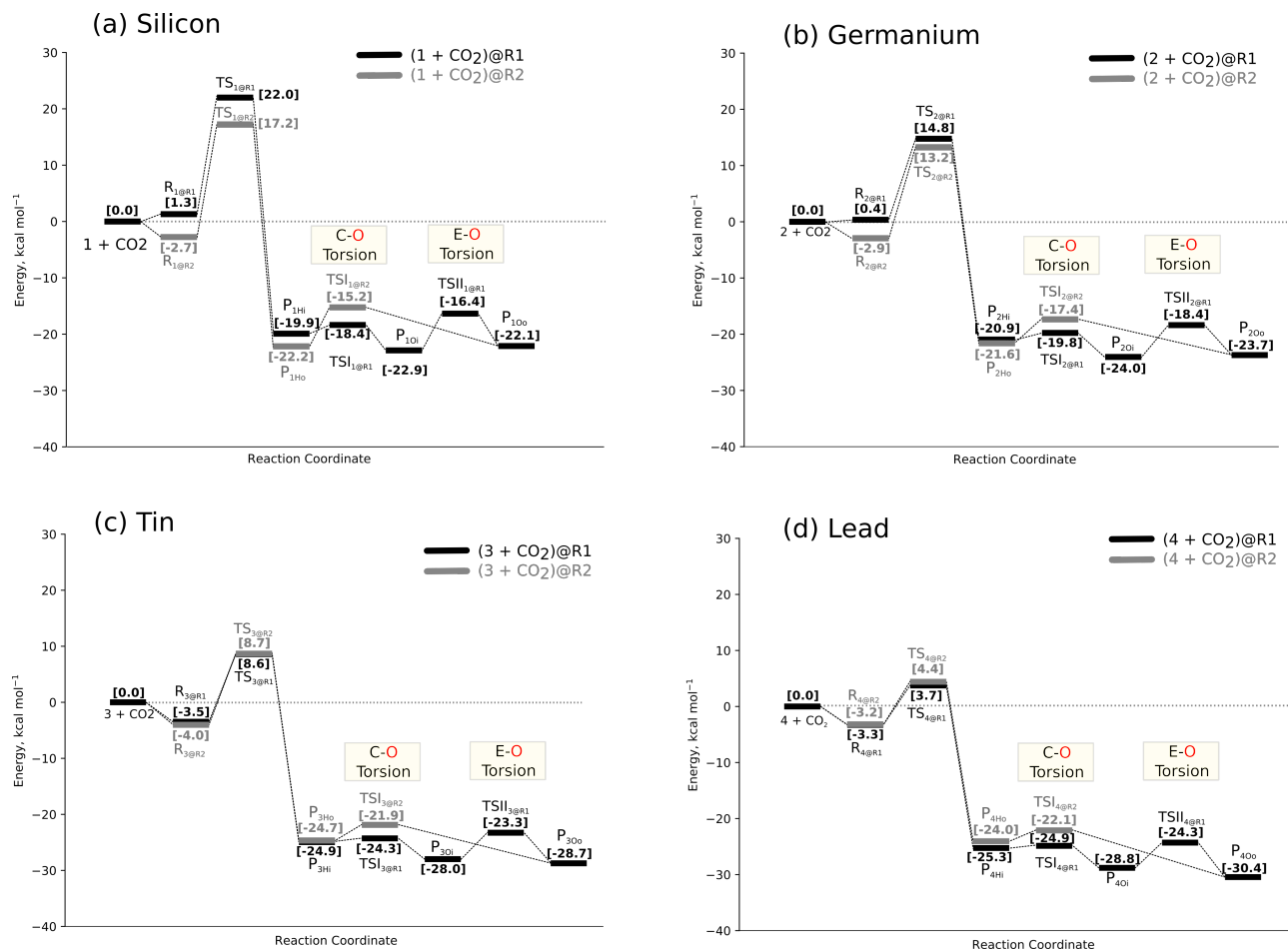


FIGURE 2.12: Potential energy surface (in kcal mol^{-1}) for the front- and back-side reactions of MG-hydride complexes with CO_2 ; (a) silicon, (b) germanium, (c) tin and (d) lead. Interconversion to different conformational stereoisomers are also shown: torsion around C–O and E–O bonds. Note that displayed values are relative to the $\text{E} + \text{CO}_2$ isolated reactants. All energies are given in kcal mol^{-1} , computed in toluene and corrected with zero point energies.

The computed relative stabilities of the new “inside” rotamers PEO_i are enhanced by 3.0 (Si), 3.1 (Ge and Sn) and 3.5 (Pb) kcal mol^{-1} with respect to the PEH_i rotamers; while the “outside” PEO_o are more stable than their PEH_o conformers as going down in group 14: -0.1 (Si), 2.1 (Ge), 4.0 (Sn) and 6.4 (Pb) kcal mol^{-1} . Thus, all rotamers are thermodynamically favored once the CO_2 reduction is carried out. Analogously, PEO_i and PEO_i conformers are obtained from low to barrierless rotations: 1.5 (Si), 1.1 (Ge), 0.6 (Sn) and 0.4 (Pb) kcal mol^{-1} . The crystal structure

reported for the stannylene formate corresponds to the conformational stereoisomer **P₃O_o** [33], which our calculations confirm as the most stable stereoisomer. Finally, Figure 2.12(d) shows evidence that our theoretically predicted plumbylene formates, **P₄O_i** and **P₄O_o**, are more stable than their sylilene, germylene and stannylene analogues being **P₄O_o** the most stable among all conformers. Therefore, this thermodynamic driving force strengthens the fact that lead(II) hydride complex seems to be a more convenient alternative for CO₂ activation than the other congeners in group 14.

2.3.2 Completing the Catalytic Cycle: The Hydroboration Step

In this section, the second step in the catalytic transformation of CO₂ is presented. As for the CO₂ activation step, the hydroboration mechanism takes place under a σ -bond metathesis regime (Figure 2.13). The main importance of this step is the recovery of the catalyst and the formation of the dioxaborolane formate.

As shown in the preceding section, Roesky *et al.* synthesized Ge(II) and Sn(II) hydride catalysts using the bidentate N-arylisopropyl β -diketiminate ligand (L¹EH in Figure 2.14) which showed a great reactivity toward CO₂ activation in toluene at room temperature [18, 32, 33]. Interestingly, the reaction of complexes L¹GeH and L¹SnH cleanly reacts toward CO₂ activation without the use of any cocatalyst to afford the respective formates L¹EOC(O)H (E = Ge, Sn) [18, 32, 33]. Following this stage, a hydride source is needed to restore the catalyst. Although reduction of CO₂ by B–H bonds and without a catalyst can be traced from the 1950s [102, 103], hydroboration of CO₂ with even the most reactive BH₃ adducts is carried out in presence of a catalyst [104–113].

Reaction of L¹GeOC(O)H with lithium aminoborane (LiH₂NBH₃) in THF at room temperature restores **2** and yield lithium formate LiOC(O)H in quantitative yield [114]. Treatment of LiOC(O)H with HCl easily produces produces formic acid. Moreover, the reaction 1:1 of L¹GeOC(O)H and H₃NBH₃ can also be carried out, but higher temperature is needed, most probably due to the low solubility of H₃NBH₃ [114]. Interestingly, the same reaction using three eq. of H₃NBH₃ gives the corresponding methanol derivate (H₃NH₂BOMe), that posterior workup with deuterated water produces MeOD [114]. Driess *et al.* used complexes L¹GeH and L²GeH (Figure 2.14) for the reaction with CO₂ giving the corresponding germylene formates, which after reaction with three eq. AlH₃NMe₃ and workup with water gave methanol. Interestingly, formation formic acid was not reported by the authors [115]. Jones *et al.* synthesized L³GeH and L³SnH (Figure 2.14). In a

first study, these compound were used to hydroborate ketones with HBpin [21]. It is worth noting that reactions with the tin-analogues were much faster than the reactions with the germanium-based complex, which may give hints of trends in reactivity along group 14. Later on, L^3GeH and L^3SnH were used for reduction of CO_2 to methanol equivalents with impressive turnover frequencies [116]. Computations performed in that study concluded that hydroboration of the formate $\text{L}^3\text{GeOC(O)H}$ to HCOOBpin corresponded to a dead end of the reaction toward the desired formation of the methanol intermediates. Computationally, Takagi and Sakaki [68] proposed the use of SiF_3H as hydride-source with $\text{L}^1\text{GeOC(O)H}$ to restore the catalyst yielding HCOOSiF_3 .

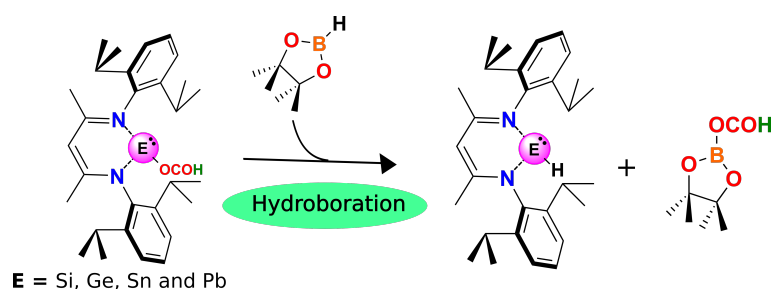


FIGURE 2.13: Hydroboration of formates with HBpin reagent. Bond insertions are schematized in color-code.

In this section, we shed light on the mechanism for the hydroboration of CO_2 by L^1GeH ($\text{E} = \text{Si, Ge, Sn, and Pb}$) toward the formation of the formic acid derivative HCOOBpin . The whole catalytic cycle (Figure 2.1) has been computed for each catalyst using density functional theory (DFT). Our intention in this contribution is to study a possible periodic trend in reactivity along the group 14 catalysts, together with a complete characterization of reactions intermediates and conformers that can be obtained in the potential energy surface for this particular reaction. Characterization of reactive reaction intermediates for the hydroboration step shall be studied in detail to comprehend the type of interactions that rule the transient viability of these species.

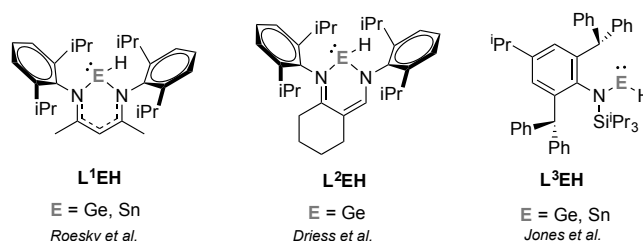


FIGURE 2.14: Relevant low valent Ge and Sn compounds.

From the conformational analysis performed in section 2.3.1.3, it is clear that for the hydroboration step, the approach of HBpin has to be studied for each of the conformers already found: **PEH_i**, **PEH_o**, **PEO_i** and **PEO_o**. As a result, it was found that for the formation of **PEH_i** and **PEO_i** formates, CO₂ should approach the catalyst (in this case the **E–O** bond) for the front-side in order to carry out the σ –bond metathesis reaction. However, due to strong steric repulsions among the methyl groups in HBpin and the *i*Pr groups in the NacNac ligand, the σ –bond metathesis is not possible as shown at the left-bottom part of Figure 2.15. In contrast to this, to prove that the steric repulsions are responsible for the not occurrence of this reaction pathways, methyl groups in HBpin were changed by hydrogens, in which a proper TS structure is successfully found (See right-bottom part of Figure 2.15). In Figure 2.15, the occurrence of each reaction with HBpin is summarized together with the representation of the TS structures³. Thus, for the hydroboration step were only considered the reaction pathways of both **PEH_o** and **PEO_o** formates with HBpin. In the next section, we explore the full reaction pathway for the transformation of CO₂ with special emphasis on the hydroboration step.

³Although a collection of transition states were found with the non-methylated HBpin reagent, these are not considered in this study.

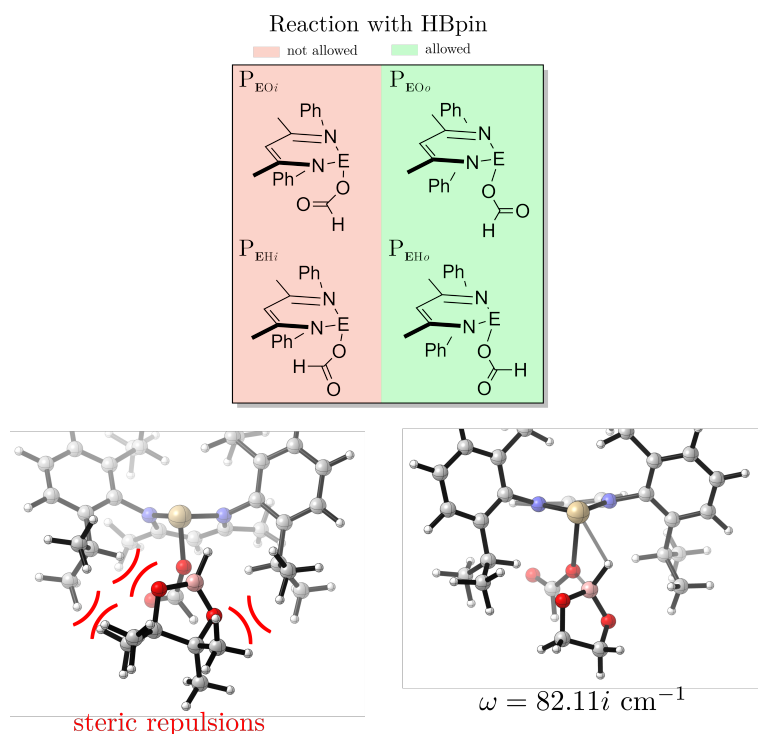


FIGURE 2.15: Resume of occurrence of reactions with HBpin (top). Schematic representation of steric repulsions in **P_{EOi}** + HBpin system (bottom left) and TS structure for the non-methylated HBpin with **P_{EOi}**.

2.3.2.1 Analysis of Reaction Pathways

In this section, results and discussions regarding the full catalytic cycle for the hydroboration of CO₂ via the low valent MG catalyst is presented (Figure 2.1). The whole catalytic cycles for Si(II), Ge(II), Sn(II), and Pb(II) catalysts are shown in Figures 2.17, 2.18, 2.20 and 2.21, respectively. For all energy profiles, key structures are shown. Furthermore, the activation, conformation and hydroboration steps were labeled along the energy profile in order to have a complete characterization of the PES.

For comparison purposes, the uncatalyzed HBpin+CO₂ reaction has been computed and shown in Figure 2.16. The reaction takes place under a one-step regime, through a four-membered TS. Due to the relative stability, ease of synthesis, and high selectivities, HBpin and HBcat (cat = 1,2-O₂C₆H₄) have emerged as candidates of the family of the dioxalborolanes. However, high temperatures are

uncatalyzed reaction							
HBpin+CO ₂		$\Delta G^\ddagger = 38.3 \text{ kcal mol}^{-1}$		$\Delta G^\circ = -15.0 \text{ kcal mol}^{-1}$			
catalyzed reaction							
MG	Path	$\Delta G^\ddagger_{CO_2}$	Product	$\Delta G^\ddagger_{LA}$	$\Delta G^\ddagger_{Hydrob.}$	$\Delta G^\ddagger_{HB}$	$\Delta G^\ddagger_{total}$
Si	Si-R1/Oo	21.0	P _{1Oo}	...	23.3	...	50.0
Si	Si-R2/Ho	21.8	P _{1Ho}	...	22.3	...	44.3
Ge	Ge-R1/Oo	15.7	P _{2Oo}	7.9	8.5	0.7	36.7
Ge	Ge-R2/Ho	21.2	P _{2Ho}	...	19.5	...	40.7
Sn	Sn-R1/Oo	12.2	P _{3Oo}	3.3	4.8	0.6	23.1
Sn	Sn-R2/Ho	14.7	P _{3Ho}	...	15.0	0.6	30.3
Pb	Pb-R1/Oo	7.9	P _{4Oo}	4.7	0.6	0.8	17.8
Pb	Pb-R2/Ho	6.5	P _{4Ho}	5.0	3.9	1.2	15.8

TABLE 2.2: Activation energies for CO₂ activation ($\Delta G_{CO_2}^\ddagger$) and hydroboration ($\Delta G_{LA}^\ddagger$, $\Delta G_{Hydrob.}^\ddagger$, and $\Delta G_{HB}^\ddagger$). $\Delta G_{total}^\ddagger$ represents the total activation energy for the whole catalytic cycle from reactants to products in the forward direction. Gibbs free energies in toluene are reported in kcal mol⁻¹.

frequently required which promotes decomposition of the borane, into BH₃-like intermediates, resulting in several organoborane products [117]. Activation and reaction free energies (taking as reference the reactant complex) were found to be 38.3 and -15.0 kcal mol⁻¹, respectively. The high activation barrier of this reaction explains why its realization under mild reaction conditions is challenging. The high activation energy for this transformation (and the σ -bond metathesis reactions studied in this work) is because they take place under a highly constrained four-membered TS and therefore the use of a catalyst is mandatory. Gibbs free energy for the uncatalyzed and catalyzed reactions are reported in Table 2.2. Reaction pathways are represented by **E-Ri/Ho** and **E-Ri/Oo** (**E** = **Si**, **Ge**, **Sn**, and **Pb**; **i** = **1** or **2**; **Ho** and **Oo** follow the spatiality of the formate).

The whole catalytic cycle for the silicon derivative, the lightest MG element in the studied series, is shown in Figure 2.17. Although the NacNacSiH has not been prepared yet, derivatives stabilized by TM compounds have been reported [59?]. Activation free energies for the incorporation of CO₂ into the **E-H** bond were found to be 21.0 and 21.8 kcal mol⁻¹ for the **R1** and **R2** paths, respectively.

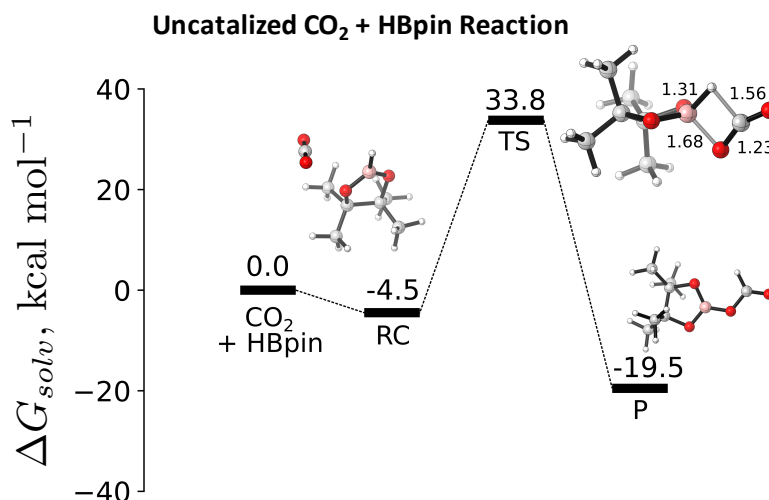


FIGURE 2.16: Energy profile for the reaction between CO₂ and HBpin. Gibbs free energies in toluene are reported in kcal mol⁻¹.

After the conformational step it can be seen that formation of the reactive complexes **P**_{1Oo}+HBpin and **P**_{1Ho}+HBpin are favored thermodynamically with ΔG° values of -27.7 and -27.8 kcal mol⁻¹, respectively. For the hydroboration step, a single TS is observed for both reaction pathways. Structures for the hydroboration step are represented by **E**-Ho or **E**-Oo in subscript ($E = 1$ (Si), 2 (Ge), 3 (Sn) and 4 (Pb); Ho and Oo follow the spatiality of the formate). Accordingly, transition states are labeled as **TSIII**_{E-Ho} and **TSIII**_{E-Oo} for **P**_{EHo} and **P**_{EOo} formates, respectively. A four-membered ring characterizes the main TS structure for the hydroboration step (**E**-O-B-H), which includes the formation of the **E**-H and B-O bonds and the breaking of the **E**-O and B-H bonds. Gibbs free energies of activation, computed taking as reference the reactant complex between the formate and HBpin for the Oo and Ho pathways, are very close to each other, 23.3 and 22.3 kcal mol⁻¹, respectively. This result suggests that a more likely path cannot be established, and thus both pathways are expected to take place.

Furthermore, it is worth noting that the activation barriers for the hydroboration step are also close to that of the corresponding CO₂ activation step. Bond distances within the four-membered ring at the TS structures are quite similar when

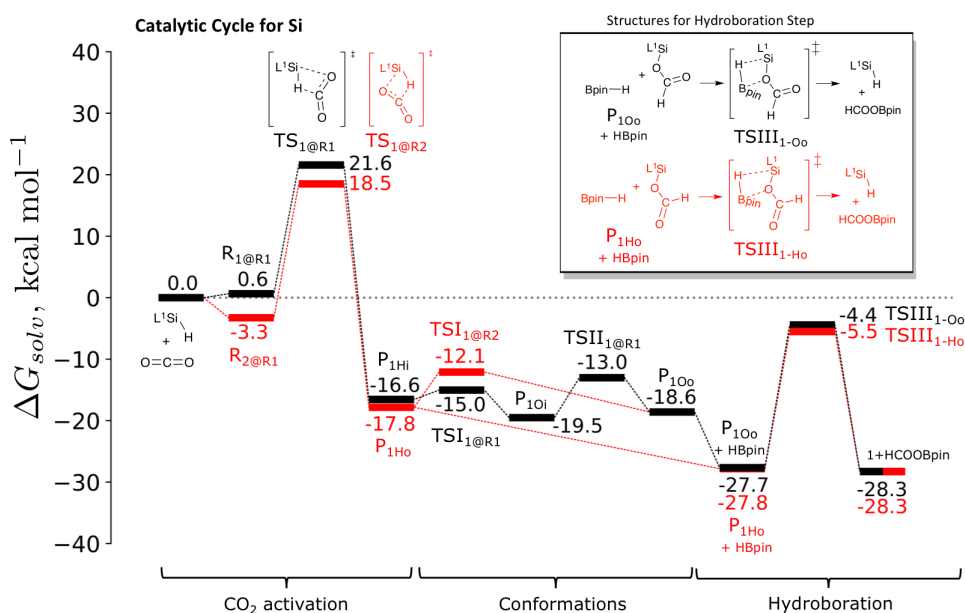


FIGURE 2.17: Gibbs energy profile for the catalytic hydroboration of CO₂ by the low valent Si catalyst (**1**). **Si-R1/Oo** and **Si-R2/Ho** pathways are represented in black and red, respectively. Energies are reported in kcal mol⁻¹ using toluene as solvent.

comparing the two reaction paths, with discrepancies of only 0.01 Å on average. It is worth noting that the activation energy for the whole activation free energy for the catalytic cycle is higher than the uncatalyzed reaction between HBpin and CO₂. The reason is due to the large dissociation energies (D_{298}°) of the Si–H (in complex **1**) and Si–O (in **P**_{1Ho} and **P**_{1Oo}) bonds, 70.1 kcal mol⁻¹ and 191.1 kcal mol⁻¹, respectively [118].

Overall, considering the appearance of a relatively high activation barrier for both the CO₂ activation and hydroboration steps, the reaction may be possible but less likely to take place at room temperature and using low pressures of CO₂.

In the case of the experimentally available Ge(II) based complex [18, 32], activation free energies of 15.7 and 21.2 kcal mol⁻¹ were obtained for the **R1** and **R2** reaction paths in the CO₂ activation step. The hydroboration of CO₂ toward formic acid derivatives is thought to be a stoichiometric 1:1:1 reaction in CO₂, catalyst, and

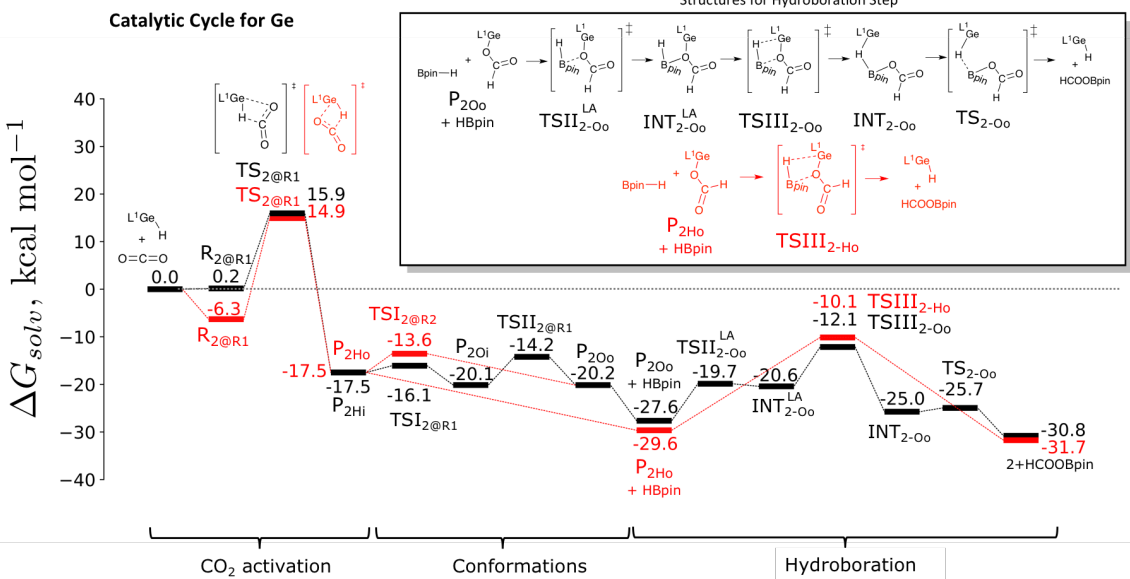


FIGURE 2.18: Gibbs energy profile for the catalytic hydroboration of CO₂ by the low valent Ge catalyst (**2**). **Ge-R1/Oo** and **Ge-R2/Ho** pathways are represented in black and red, respectively. Energies are reported in kcal mol⁻¹ using toluene as solvent.

HBpin, respectively. Interestingly, Jones *et al.* [21] reported no noticeable reactions between L³GeH or L³SnH hydride with HBpin, as a result of favorable acid-base Lewis interactions. It was observed that the particular low field hydride resonance (¹H NMR) of the complexes is only negligibly shifted after addition of HBpin to the solution containing the catalyst. We studied the Lewis acid-base interaction between **2** and HBpin, and we have found that the lone pair over Ge(II) and Sn(II) is sterically protected from reacting with the empty *p*-orbital on the boron atom. Interestingly, the hydroboration step for the germanium analog shows noticeable differences between the Ho and Oo reaction pathways (Figure 2.18).

As for silicon, the Ho reaction channel exhibit a single TS for the hydroboration of CO₂ with an activation free energy of 19.5 kcal mol⁻¹. On the other hand, the Oo pathway is carried out under a multi-step regime. First, as HBpin approaches the formate complex, a favorable B···O interaction takes place, giving rise to the formation of a Lewis Adduct (LA) intermediate (**INT**_{2-Oo}^{LA}) with an activation free energy of 7.9 kcal mol⁻¹. The **INT**_{2-Oo}^{LA} system is formed with a B–O distance of

1.68 Å (bond order 0.47). After the appearance of the LA intermediate, formation of the Ge–H bond and breaking of the Ge–O bond start to take place, giving rise to **TSIII**_{2-Oo}. From **INT**_{2-Oo}^{LA} to the formation of **TSIII**_{2-Oo}, the strengthening of the B–O bond and the weakening of the B–H and Ge–O bonds take place. At **TSIII**_{2-Oo} the B–O distance is decreased from 1.68 (in **INT**_{2-Oo}^{LA}) to 1.55 Å (89% of formation with respect to the product structure). The Gibbs free energy of activation from the LA intermediate to the rate-limiting TS structure is just 8.5 kcal mol^{−1}. For this path, the activation barrier of the whole hydroboration process, considered as the sum of $\Delta G_{\text{LA}}^\ddagger$ and $\Delta G_{\text{Hydrob.}}^\ddagger$, is 16.4 kcal mol^{−1}, which is more favored compared with the concerted Ho path (19.5 kcal mol^{−1}). Interestingly, the B–H bond does not change considerably from **INT**_{2-Oo}^{LA} to **TSIII**_{2-Oo}. Afterward, the Ge–O bond is broken, and a favorable Ge⋯H⋯B cooperative interaction gives rise to a reactive H-bridged intermediate **INT**_{2-Oo}. At **INT**_{2-Oo}, the Ge⋯H⋯B interaction corresponds to a three-center two-electron (3c–2e) interaction. In the **INT**_{2-Oo} species, the Ge–H and B–H bond distances are 1.75 and 1.45 Å, respectively. Special attention to **INT**_{2-Oo}^{LA} and **INT**_{2-Oo} intermediates will be given later in this work. Moreover, it is worth to note that the low activation free energies of **TSII**_{2-Oo}^{LA} and **TS**_{2-Oo} toward **PEOo** + HBpin and **2** + HCOOBpin, respectively, are visualized as shoulders appearing in the PES, due to its low activation energies (see for example Figure 2.22(a) for the step represented by $\Delta G_{\text{HB}}^\ddagger$).

In a mixed experimental-computational study, Maron and Jones *et al.* reported the use of L³GeH and L³SnH hydrides for the reduction of CO₂ to methanol equivalents (MeOBR₂) by using HBpin or HBcat as hydride source [116]. DFT computations proved that a respective μ -bridge intermediate is formed with activation energies close to 1 kcal mol^{−1}, recovering the catalyst and giving HCOOBpin. Instead of a 4-membered TS as reported here, they proposed a 6-membered TS. In Figure 2.19, a summary of the reactions using L¹GeH and L³GeH with representation of the respective TSs is presented and used for discussion. Through the formation of the 6-membered TS, the authors [116] reported a low activation enthalpy of 2.2 kcal mol^{−1} compared to a larger activation free energy reported in the present

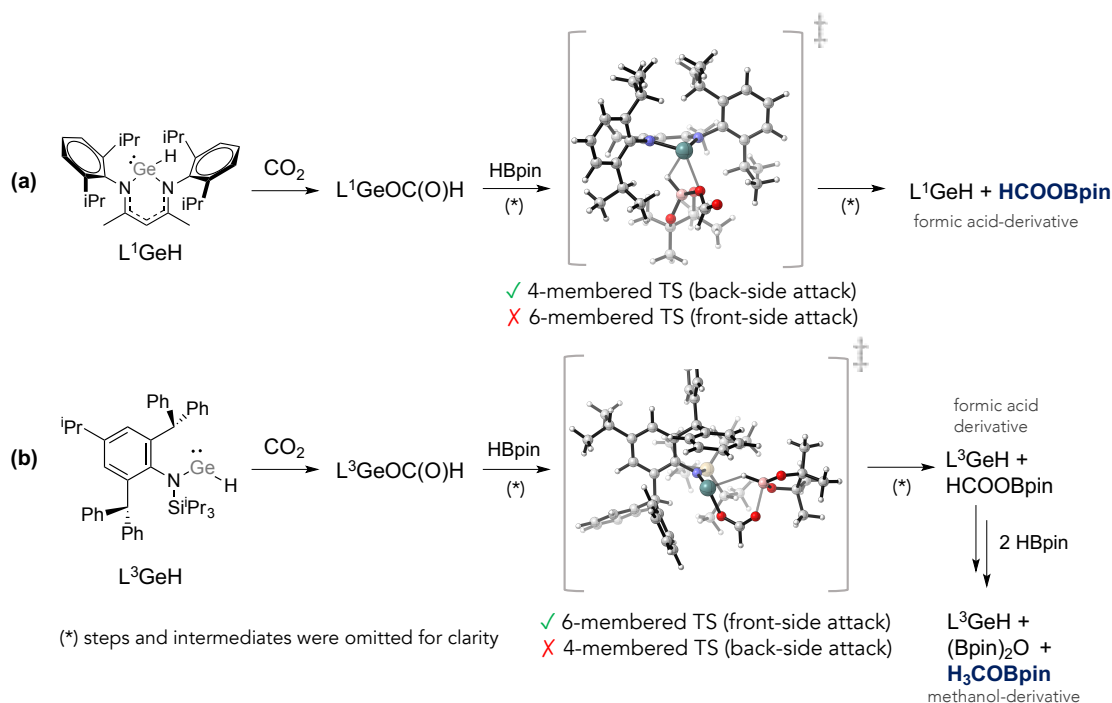


FIGURE 2.19: Schematic representation for the hydroboration of CO₂ using (a) L¹GeH and (b) L³GeH. Transition state structures for the hydroboration step for both catalysts are also shown.

contribution of 16.4 kcal mol⁻¹. This energetic difference reveals a big difference in structure-reactivity differences between mono- and bidentate ligands.

Motivated by the results of Maron and Jones, we studied the occurrence of the 4- and 6-membered TS using L¹GeH and L³GeH. We found that the catalyst's design prevents the formation of a 6-membered (4-membered) TS when the L¹GeH (L³GeH) catalyst is used. Let us define the position of the formate (–OCOH) unit as the *front-side*. For the L¹GeH complex a 6-membered TS is not possible due to the bidentate ligand retains the Ge atom in position. Thus the Ge–O–C angle in the formate complex prevents its change as the 6-membered formation comes into effect (the bidentate ligand firmly maintains the pyramidal geometry in Ge; see **P20o** in Figure 2.12(b) for reference). Furthermore, the bulkiness of both the HBpin and ⁱPr groups in the NacNac ligand also helps prevent the 6-membered TS. Regarding the L³GeH catalyst, it is clear from Figure 2.19(b) that the *back-side* approach is blocked by the –CH(Ph)₂ and –SiPr₃ moieties in the L³ ligand.

According to Maron and Jones [116], after the formic acid-derivative is formed, HCOOBpin reacts again with the L³GeH and in several stages using 2 more equivalents of HBpin to yield the methanol derivative CH₃OBpin and (Bpin)₂O (Figure 2.19(b)). The reaction of L¹GeH toward the formation of methanol derivatives with HBpin is under active research in our group. We believe that a control in the selectivity toward formic acid, formaldehyde, and methanol equivalents can be done by means of changes in stoichiometry, identity (bulkiness or reductant strength) of the hydride-source, the nature (steric demand and denticity) and catalytic loadings of the catalyst as previously reported for Ni and Pd catalysts [119].

In summary, the formation of formic-acid or methanol derivatives with Ge(II) hydrides (and extended to other catalysts) is subject to the stoichiometry of the reaction. Moreover, it can be concluded that the denticity and bulkiness of the ligand establish the appearance of a 4- or 6-membered TS.

On the other hand, the experimentally obtained tin-containing complex [18, 33] can reduce even more the activation energy for the CO₂ capture, as the Sn–H bond becomes more polarizable than the Ge analog [120]. Gibbs free energies of activation for the reaction pathways, **R1** and **R2**, are very close, namely 12.2 and 14.7 kcal mol⁻¹, respectively. As may be noticed, activation energies involving complex **3** are lower than that obtained for complex **2**, thus attributing faster conversion when using tin-derivatives than germanium, as observed experimentally [21, 116]. With regard of the hydroboration step, it can be seen that the same mechanism for the lighter Ge(II) congener takes place on the Oo pathway, but different to that for the Ho path. For tin, the Ho pathway does not exhibit the formation of the Lewis adduct, **INT**_{3-Oo}^{LA}. For both pathways, formation of the Sn–H bond and breakage of the Sn–O bond through the **TSIII**_{3-Ho} ($\Delta G^\ddagger = 15.0$ kcal mol⁻¹) and **TSIII**_{3-Oo} species ($\Delta G^\ddagger = 8.1$ kcal mol⁻¹ from the reactive complex and 4.8 kcal mol⁻¹ from the Lewis Adduct) dominates the hydroboration step. As may be observed from

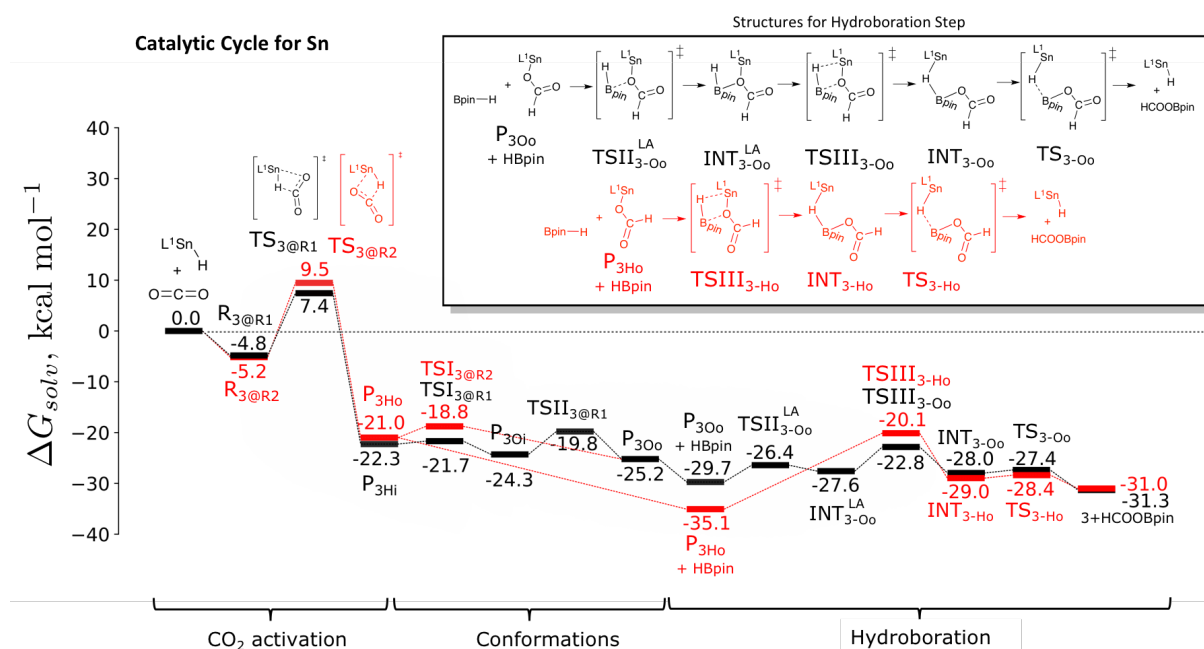


FIGURE 2.20: Gibbs energy profile for the catalytic hydroboration of CO₂ by the low valent Sn catalyst (**3**). **Sn-R1/Oo** and **Sn-R2/Ho** pathways are represented in black and red, respectively. Energies are reported in kcal mol⁻¹ using toluene as solvent.

Figure 2.20, the Oo pathway is energetically more favored than the Ho pathway through the formation of the reaction intermediates.

Finally, the most reactive complex for both activation and hydroboration of CO₂ is the computationally proposed NacNacPbH catalyst. The lead β -diketiminato halide [60], aryloxyde [62], phosphanide [64], alcoxide [61, 64, 65], alkyl [66], amido [61, 63], anilido [63], among other derivatives, have been prepared, but complex **3** has not been obtained to date. Recently, efforts made by the groups of Wasserman and Power have shown the first low valent lead hydride compounds using monodentated ligands [121, 122]. Activation energies for the CO₂ activation step are 7.9 and 6.5 kcal mol⁻¹ for **R1** and **R2**, respectively. In the hydroboration step, both reaction pathways exhibit the formation of the LA and H-bridged intermediates that promote a more feasible way for the transformation of CO₂. For the Ho pathway, the activation energy involving **TSIII**_{4-Ho} amounts to 8.9 kcal mol⁻¹ ($\Delta G_{LA}^{\ddagger} + \Delta G_{Hydrob.}^{\ddagger}$). Furthermore, for the Oo path the total activation energy

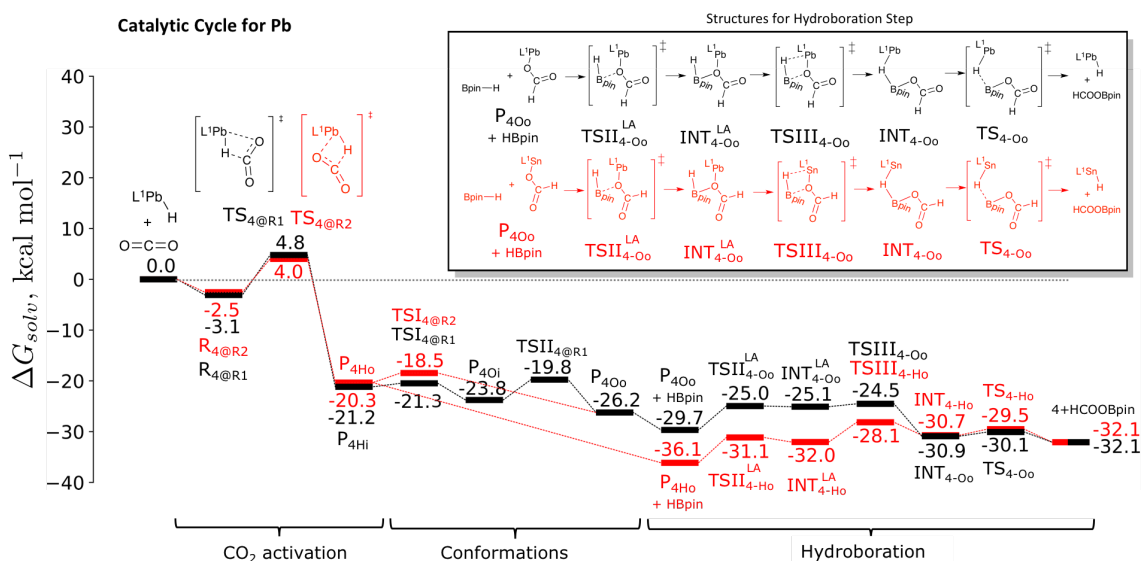


FIGURE 2.21: Gibbs energy profile for the catalytic hydroboration of CO₂ by the low valent Si catalyst (4). **Pb-R1/Oo** and **Pb-R2/Ho** pathways are represented in black and red, respectively. Energies are reported in kcal mol⁻¹ using toluene as solvent.

involving **TSIII**_{4-Oo} is even lower with 5.3 kcal mol⁻¹.

Activation energies for the σ -bond metathesis in the activation and hydroboration of CO₂ from Ge to Pb were found to be low enough –below 22 kcal mol⁻¹– and therefore the process is highly feasible to take place under mild reactions conditions. For comparison purposes, the free activation energy of 38.3 kcal mol⁻¹ for the uncatalyzed CO₂+HBpin reaction is compared to the sum of the activation energies of the individual processes in the forward direction ($\Delta G_{total}^\ddagger$). The latter energies are collected in Table 2.2. As it was observed from the energy profiles for each catalyst, there is a noticeable decrease in the activation energies for each stage concerning the uncatalyzed reaction. However, taking the total activation energies for each catalytic cycle, it can be seen that a sufficient reduction of the total activation energy, $\Delta G_{total}^\ddagger$, is observed from the germanium analog (only Oo pathway) being more favored going down in group 14 (both reaction pathways). More interestingly, the lead-derived complex **4** can decrease the total energy barrier less than one-half when compared to the uncatalyzed reaction.

In Summary, we have shown evidence that the catalytic process becomes more effective with regards to activation energies as we move down group 14, in which an apparent decrease (compared to the uncatalyzed reaction) of the activation energy can be observed just from the germanium derivative **2**. Moreover, from these results, it is concluded that the decrease of the activation energies is directly attributed to the effect of the central low valent group 14 element. It was also found that steric demand and denticity of the ligand can determine the type of TS (4- or 6-membered TSs) in the hydroboration step.

2.3.2.2 Characterization of $\text{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\text{INT}_{2-\text{Oo}}$

In this section, the germanium reaction intermediates were chosen as representatives of the whole set of reactions. Bonding features, as well as interactions that lead to the formation of the LA and H-bridged intermediates, are studied in great detail.

First, to corroborate the appearance of the reaction intermediates and to ensure that they were not obtained as an artifact of the density functional used in the present work, a benchmark study was done (see Appendix E). Over 20 DFT functionals were used, encompassing pure, hybrid, hybrid meta-GGA and long-range corrected functionals. Interestingly, it was found that functionals that do not include dispersion corrections are not able to reproduce both $\text{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\text{INT}_{2-\text{Oo}}$, yielding the reactive complex or product structure (for $\text{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\text{INT}_{2-\text{Oo}}$ optimizations, respectively). Clear examples of the later findings are the ones computed with B3LYP and APF functionals that converged to the desired intermediates once the dispersion correction is taken into account (B3LYP-D3BJ and APFD). On the other hand, most of Minnesota functionals can reproduce both reaction intermediates. Therefore, the inclusion of dispersion corrections are necessary to have a full characterization of relevant structures along the reaction mechanism.

As mentioned above, the LA-intermediate is formed from the interaction of the Lewis acidic boron atom of HBpin and the oxygen atom in the formate complex. The H-bridged intermediate instead is formed from the cooperative $3c-2e$ $\text{Ge}\cdots\text{H}\cdots\text{B}$ attractive interaction. As $\text{INT}_{2-\text{Oo}}$ exhibits the $\text{Ge}\cdots\text{H}\cdots\text{B}$ interaction, both B–H breaking and Ge–H bond-breaking reaction paths were studied. In Figure 2.22, the two reaction paths are depicted along with relevant structures. If the B–H bond in $\text{INT}_{2-\text{Oo}}$ breaks, a low activation energy allows the formation of the desired reaction products: **2** + HCOOBpin (neutral path, Figure 2.22(a)). On the contrary, if the Ge–H bond breaks, it would lead to the formation of ionic

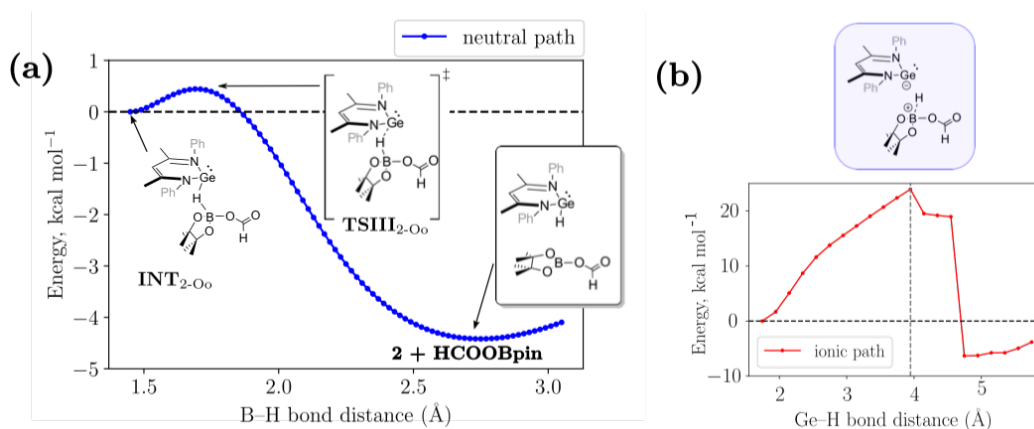


FIGURE 2.22: (a) Energy profile along B-H bond distance (neutral path) and energy along Ge-H bond (ionic path). For both reaction pathways relevant structures are presented.

species (ionic path, Figure 2.22(b)). Undoubtedly, the neutral path is preferred. In the ionic path (Figure 2.22 (b)), as the Ge-H bond distance increases, the energy does so almost linearly. At $d_{\text{Ge-H}} = 3.96 \text{ \AA}$ ($\Delta E = 23.9 \text{ kcal mol}^{-1}$) convergence problems arise as the charged species are far apart. However, this is enough evidence to conclude that there is no competition among the neutral and ionic paths. Therefore, the B-H bond breaking in **INT**_{2-O_o} is by far the preferred mechanism.

To characterize noncovalent interactions (NCIs) that may be driving the precarious stabilization of these intermediates, the NCI analysis of Johnson and co-workers was employed [123, 124]. Molecular representations of **INT**_{2-O_o}^{LA} and **INT**_{2-O_o} with the NCI isosurface are shown in Figure 2.23. From the molecular representations, it may be seen that both CH/CH and CH/ π van der Waals interactions (green surfaces) help favor these transient species. In the **INT**_{2-O_o}^{LA} system, a strong, attractive interaction (blue) is found between the germanium and oxygen atoms in the Lewis adduct moiety, most probably due to strong Coulombic interactions between Ge and O atoms. Inspection of NBO charges shows a large charge separation between Ge and O with charges $1.30 |e|$ and $-0.84 |e|$, respectively. On the other hand, for **INT**_{2-O_o}, blue surfaces appear in the Ge-H and B-H bonds, revealing highly attractive interactions. Inspection of charges show that the hydride (-0.32

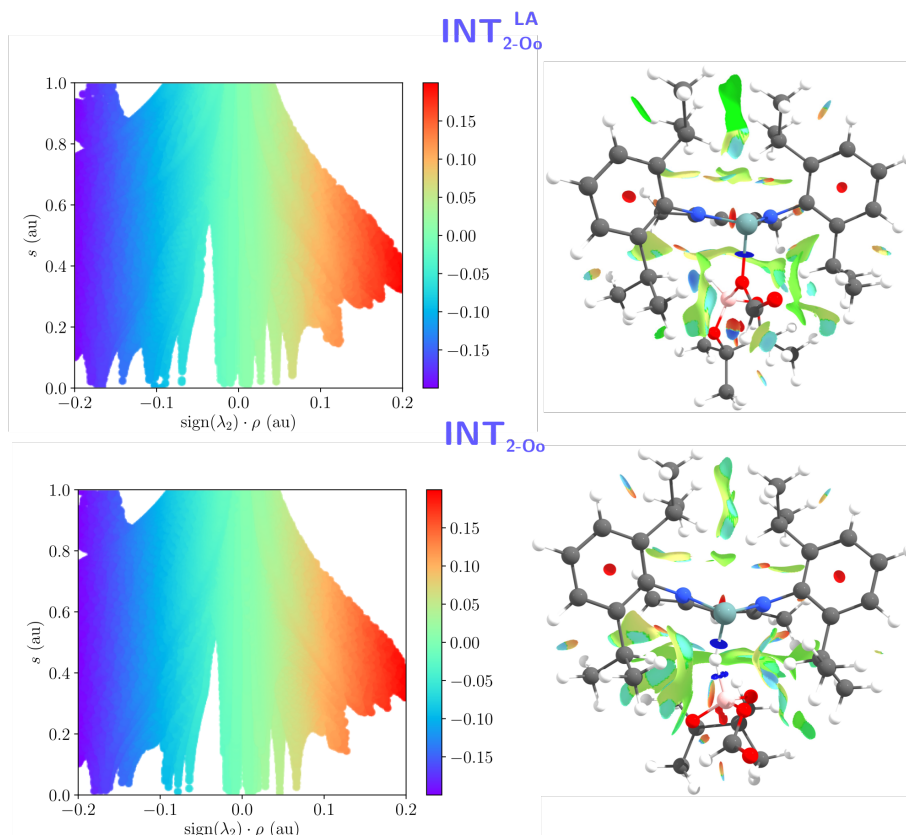


FIGURE 2.23: Noncovalent interaction (NCI) analysis of intermolecular interactions in color-code.

$|e|$) is stabilized electrostatically by the positive charged Ge ($1.17 |e|$) and B ($1.20 |e|$) centers. The Ge–H and B–H bond orders are 0.48 and 0.53, which show the partial formation of these bonds and allowing a total bond order over the hydride of 0.9, which is consistent with a $3c-2e$ bond.

With the aim of giving a quantitative characterization of the noncovalent interactions, SAPT0 computations [86] were performed on the $\text{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\text{INT}_{2-\text{Oo}}$ species. As summary of the main physical components of the SAPT interaction energies, together with fragmentation used, is shown in Figure 2.24. The total interaction energies between the fragments for the Lewis and H-bridged intermediates are -38.1 and $-35.1 \text{ kcal mol}^{-1}$, respectively. For $\text{INT}_{2-\text{Oo}}^{\text{LA}}$, the main noncovalent interactions are primarily electrostatic, although induction and dispersion also contribute in that order. As a result of the $\text{B} \cdots \text{O}$ bond formation,

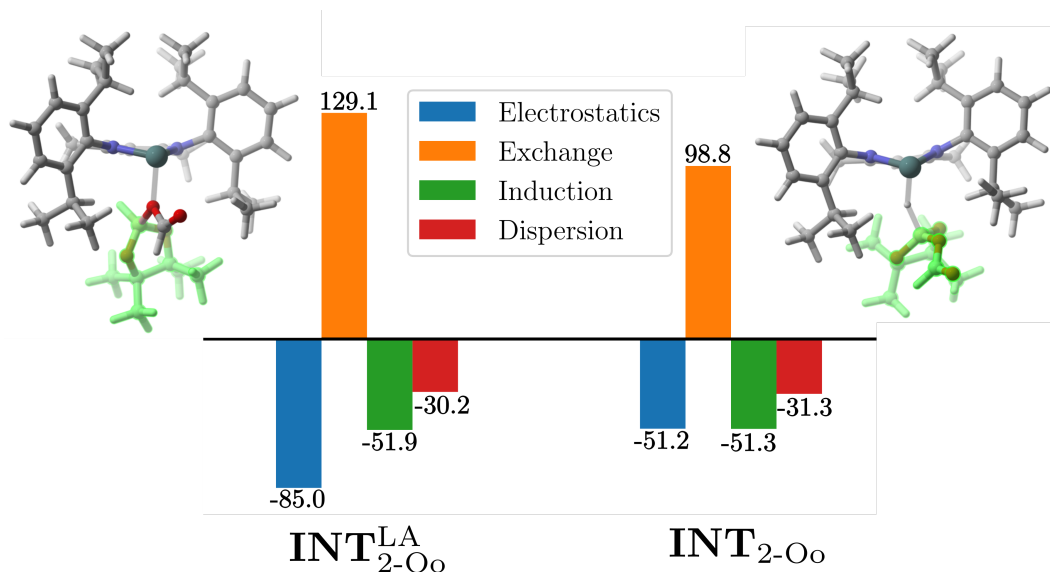


FIGURE 2.24: SAPT0 analysis for $\text{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\text{INT}_{2-\text{Oo}}$ intermediates. Energies are given in kcal mol^{-1} .

polarization and charge transfer between fragments can be measured from the induction term. It was found that polarization ($-29.6 \text{ kcal mol}^{-1}$) is more significant than charge transfer effects ($-22.3 \text{ kcal mol}^{-1}$) at this geometry. To study the strong Coulombic interaction revealed by the NCI results, a partition of the Ge–O bond was studied. In this partition, the electrostatic term increases to $-135.4 \text{ kcal mol}^{-1}$. For the $\text{INT}_{2-\text{Oo}}$ species (partition according to Figure 2.24), induction and dispersion interactions contribute equally to the transient stabilization of this species, with a less pronounced charge transfer energy ($-13.6 \text{ kcal mol}^{-1}$) but with higher polarization ($-37.7 \text{ kcal mol}^{-1}$). Since the reverse $\Delta G_{\text{LA}}^{\ddagger}$ and the $\Delta G_{\text{HB}}^{\ddagger}$ energies are so close for each group 14 center, it is believed that similar intermolecular interactions drive the transient stabilization in the remaining Si, Sn, and Pb-based intermediate.

In summary, in the LA intermediate, the oxygen atom directly attached to Ge transfers electrons to the boron atom in HBpin to form the adduct. This is evidenced with a more substantial electrostatic term and charge transfer energy. Conversely, in the H-bridged intermediate orbital and electrostatic interactions seem to favor the appearance of $\text{INT}_{2-\text{Oo}}$, but with a diminished electron transfer

from the complex to the HCOOBpin moiety through the Ge···H···B interaction.

Finally, with the aim of study the prevalence of both B···O and Ge···H···B interactions in **INT**_{2-Oo}^{LA} and **INT**_{2-Oo}, respectively, reaction dynamic simulations were computed using atom-centered density matrix propagation molecular dynamics model (ADMP)⁴. A total of 20,000 conformations in a time of 2.0 ps were used for statistics at 300 K. With the aim of saving computational time, a representative system in which *i*-Pr and methyl groups were replaced by methyl and hydrogen atoms, respectively, was chosen. Propagation of bond distances between atom *a* and *b* are studied by the pair distribution function $g_{ab}(\mathbf{r})$ which determines the distribution of distances between pairs of atoms along the trajectory.

In Figure 2.25, the $g_{ab}(\mathbf{r})$ function for **INT**_{2-Oo}^{LA} (B–O and Ge–O bond) and **INT**_{2-Oo} (B–H and Ge–H) species is shown. In the case of the LA intermediate, it can be seen that the Ge–O distance is centered in the range 1.90–2.08 Å while it is 2.03 Å in the gas phase. On the contrary, the B–O bond exhibit a high oscillation and therefore a great dispersion in bond length is obtained in the $g_{ab}(\mathbf{r})$ profile. Therefore, it can be seen that the Ge–O is retained over the simulation while the B–O bond, responsible for the LA interaction, collapses in some periods of time. It suggests that in the LA species the boron-oxygen Lewis interaction is not strong enough to stabilize the adduct, although dispersion forces may play a significant role on stabilization.

Regarding the **INT**_{2-Oo} species, the Ge···H···B cooperative interaction collapses after 1,000 fs in which the B–H bond breaking come into effect. The Ge–H bond length was found to oscillate mainly between 1.59 and 1.79 Å while the gas phase distance is 1.71 Å. On the contrary, an expected great dispersion of bond length was found for the B–H bond since this bond breaks. However, in the range when the Ge···H···B interaction holds (see the first peak in red color on Figure 2.25),

⁴To watch dynamic simulations click **INT**_{2-Oo}^{LA} and **INT**_{2-Oo}.

the B–H bond length is found to be in range 1.26–1.42 Å (gas phase bond distance of 1.36 Å). From the results, the Ge–H bond distance oscillates in a range around the corresponding gas-phase bond distance, since the breaking of this bond would cause an ionic path which is not likely to take place as mentioned above.

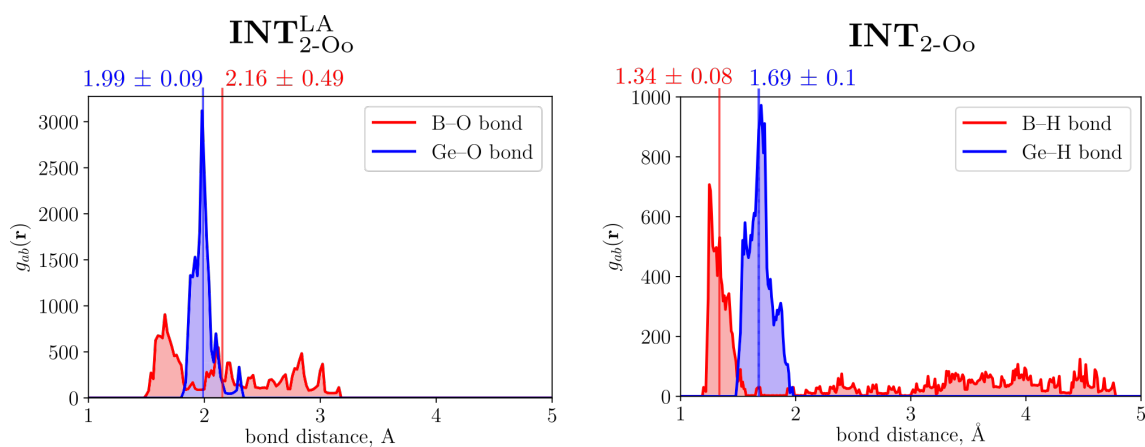


FIGURE 2.25: Radial pair distribution functions to selected bond distances for $\text{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\text{INT}_{2-\text{Oo}}$. A total of 20,000 conformations were used for statistics.

2.4 Conclusions

The CO₂ activation mechanism by low-valent Si(II), Ge(II), Sn(II), and Pb(II) hydride complexes bearing a bidentated β -diketiminato (NacNac) ligand has been studied in great detail by DFT calculations. According to the computed activation energies for the whole catalytic cycles, the Pb based complex is predicted to be (by far) the most active towards CO₂ hydroboration, followed in order by the Sn, Ge, and Si analogs: the CO₂ activation and hydroboration processes become more favorable as we descend in group 14. This trend is found as a direct consequence of the enhanced polar character of the **E**–H bond (hydrides) and **E**–O (formates), more Lewis acidic metal center, as the atomic radii of the metal increases when going down in group 14. However, when the catalytic cycle for catalysts **1-4** is compared in energetic terms with the uncatalyzed CO₂+HBpin reaction, an effective energetic decrease is observed from the germanium derivative **2**. Moreover, free energy barriers for the activation and hydroboration of CO₂ from Ge to Pb were found to be low enough –below 22 kcal mol^{–1}– and therefore the process is highly feasible to take place under mild reactions conditions.

Regarding the hydroboration step, it was found that only the **P**_{EH_o and **P**_{EO_o can make possible the hydroboration step, since the *i*-Pr groups in both **P**_{EH_i and **P**_{EO_i species prevent the approaching of HBpin. Moreover, it has been found that the reaction mechanism for the hydroboration step changes from concerted to stepwise when going down in group 14, with the appearance of two different reaction intermediates: **INT**_{E–O_o}^{LA} and **INT**_{E–O_o}. From NCI and SAPT computations we showed that in the LA intermediate, the oxygen atom directly attached to Ge transfers electrons to the boron atom in HBpin to form the adduct, which is evidenced with a larger electrostatic term and charge transfer energy. Conversely, in the H-bridged intermediate orbital and electrostatic interactions seem to favor the appearance of **INT**_{2–O_o} but with a diminished electron transfer from the complex to the HCOOBpin moiety through the Ge···H···B interaction.}}}}

In summary, although an effective catalytic decrease is observed from Ge(II) going down in the group, this computational study suggests the lead(II) hydride complex as a more convenient alternative for activation and hydroboration of CO₂. The trend in reactivity found here should aid in new developments in main group chemistry. Moreover, we have provided computational evidence that a smart choice of the steric demand of the catalyst-hydride source, together with the stoichiometry, may play an essential role in the selective formation of formic and/or methanol intermediates as recently found in TM catalysis [119]. More experimental results are needed to corroborate these findings, but these observations strongly support the intrinsic selectivity power in MG catalysts.

Chapter 3

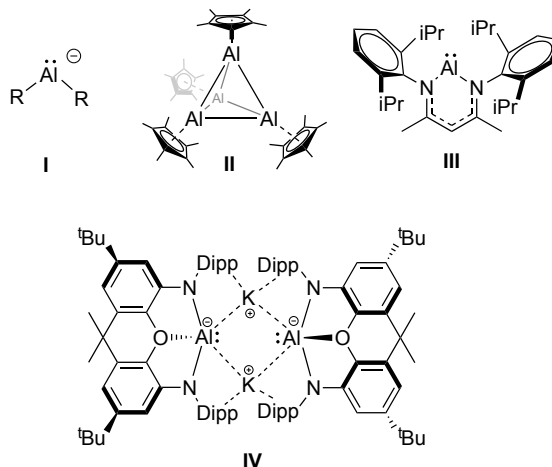
Activation of H₂ by Aluminyl Anions

3.1 Introduction

Aluminyll anions, are a class of low valent Al(I) compounds which electronic structure resembles a carbene (**I** in Figure 3.1). These chemical species have a stereochemically active electron lone pair but bearing a negative charge [27, 125–133]. One of the main disadvantages of low valent Al species (and generally in low valent main group elements) is the relatively low kinetic and thermodynamic stability, which may produce undesired disproportionation or dimerization reactions [133–135]. The very first example of aluminum(I) compound was the meta-stable mono-halide AlCl compound reported by Tacke and Schnöckel about 30 years ago [125, 136]. This experimental evidence served as inspiration for the study of low valent aluminum species. It is worth noting that AlCl is central in low valent Al chemistry since it serves as a precursor for several Al(I) ligand-stabilized compounds. Dohmeier *et al.* synthesized **II**, a parent non-carbenoid tetrameric Al(I) compound forming an Al_4 cluster with four interacting methylated cyclopentadienyl moieties [126]. The $\{Al(\eta^5-C_5Me_5)\}_4$ cluster is prepared using a solution of AlCl and $Mg(\eta^5-C_5Me_5)_2$ [126, 134, 137]. Most interestingly, in 2000, Roesky *et al.* [1] showed evidence of the first monomeric carbenoid Al(I) complex **III**. With the idea of enhancing the stability of Al(I) derivatives, the bulky N-Arylisopropyl- β -diketiminate ligand $[ArNC(Me)CHC(Me)NAr]^-$ with $Ar = 2,6-iPr_2C_6H_3$ was used for such purpose. Nowadays, different low valent main group compounds are found in literature in which the design and engineering of the ligand play a significant role in the stabilization of these species, expanding the field rapidly.

Complex **III** has been shown to activate a wide variety of robust σ -bonds and π -bonds [138–153], together with being used in oxidation reactions and the interaction with transition metals [154, 155]. To have a better understanding of the mechanism of σ -bond activation by low valent group 13 catalysts quantum chemistry calculations have also been performed [29, 148, 156]. Regarding aluminyll anions, Hicks *et al.* have reported the synthesis of **IV**, a novel potassium aluminyll catalyst using a NON xanthene-derived ligand [157]. Catalyst **IV** can activate H_2

FIGURE 3.1: Structures of the different species discussed: (I) aluminyll anion, (II) low valent Al compound Al_4X_4 , (III) low valent NacNacAl complex (NacNac = $ArNC(Me)CHC(Me)NAr$] $^-$ with $Ar = 2,6-iPr_2C_6H_3$)[1], (IV) simplest Arduengo-type Al-based compound, (V) Al(III) derivative (basic structure for hypohomodesmotic energy scheme when $R = H$) and (VI) Al(III) anion compound (basic structure for the isodesmic energy scheme when $R = H$).



in benzene solution at ambient conditions or 2 atm of this gas in the solid-state. Furthermore, activation of C–H bonds in benzene and formation of Al–Al and Al–Mg bonds has also been observed [157, 158]. Aluminum has attracted massive attention as a potential catalyst since it is the most abundant metal in the earth’s crust, together with the fact that its use has been proposed for energy production. Indeed, aluminum can activate H_2 through oxidative addition, and an eventual isothermal reductive elimination mechanism for releasing H_2 would make this element a potential candidate. Chu and Nikonov [159] have reported an excellent review on oxidative addition and reductive elimination in main group compounds.

In this chapter, the activation of H_2 by aluminyll anions is studied. The $[K\{Al(NON)\}]_2$ complex reported by Hicks *et al.* is studied toward the activation of H_2 . The dimeric and monomeric forms will be matter of interest. In particular, the possible catalytic role of the potassium atoms will be presented. Moreover, substituted aluminyll anions are used to reveal the substituent effect in geometry and electronic structure of these species. Activation of H_2 using these model systems will

be studied.

3.2 Theoretical Methods

The H_2 activation using the $[K\{Al(NON)\}]_2$ catalyst was studied using density functional theory (DFT). The hybrid meta-GGA M06-2X functional was used since it has been shown to correctly predict both kinetics and thermodynamics [69–71]. Energy was reported through single point computations at the DLPNO-CCSD(T)/def2-TZVP on the previously optimized structures at the M06-2X/def2-SVP [160–164]. The def2-SVP basis was used owing the big size of complex **IV** (144 atoms, 572 electrons, and 1432 basis functions).

The structure of substituted aluminyll anions together with the activation of H_2 , was studied using high-level coupled-cluster techniques. Equilibrium and transition state (TS) geometries were optimized employing coupled-cluster theory with single, double, and perturbative triple excitations using the augmented correlation-consistent triple- ζ basis set of Dunning, aug-cc-pVTZ[165]. The inclusion of diffuse functions is needed to correctly model electronic resonance effects as well as the larger electronic cloud that anions may exhibit. Since aluminum bears a negative charge and a stereochemically active electron pair, additional functions were employed for a good description of $3d$ -like electrons. These extra basis functions are called *tight(d)* functions. All computations required restricted Hartree-Fock wave functions (RCCSD(T)/aug-cc-pV(T+d)Z) [166, 167]. Tight convergence criteria were used for geometry optimizations, in particular RMS gradients were converged to $\leq 10^{-10} E_h a_0^{-1}$ with self-consistent field and coupled-cluster convergences of $10^{-10} E_h$. Core electrons were not correlated during the optimization procedure. After optimization, obtained geometries were confirmed by harmonic frequency computations at the RCCSD(T)/aug-cc-pV(T+d)Z level of theory. Transition states were characterized by exhibit a single imaginary frequency near 1200 cm^{-1} ,

while for minima, all frequency were positive.

Activation and reaction energies extrapolated at the complete basis set (CBS) [168, 169] were computed using the focal point approach (FPA) of Allen and co-workers [170–173]. This approach enables to compute highly accurate electronic energies by a systematic increase in correlation treatment and basis set. In this approach, the three-point formula developed by Feller was used for extrapolating HF energies [174] while Helgaker’s two-points expression was used to extrapolate post-HF energies [175], both formulas are shown in Eq. (3.1) and Eq. (3.2).

$$E_{HF}(X) = E_{HF}^{\infty} + ae^{-bX} \quad (3.1)$$

$$E_{corr}(X) = E_{corr}^{\infty} + aX^{-3} \quad (3.2)$$

In Eqs (3.1) and (3.2), X is the cardinal number in the cc-pVXZ basis corresponding to the maximum angular momentum of it. Extrapolation to the CBS limit was performed using coupled-cluster theory with single, double, triple, and perturbative quadruple excitations [CCSDT(Q)]. The frozen core (FC) approximation with the *aug*-cc-pVnT ($n = D, T, Q, 5$) basis set of Dunning were employed [165, 176–179]. For reactants, transition states and products we computed Hartree-Fock, second-order Møller-Plesset, CCSD, CCSD(T), and CCSDT(Q) single-point energies with the above-cited augmented basis sets up to $n = 5$, in addition of using extra *tight(d)* functions for the aluminum atom. Therefore, energies at CBS can be considered as CCSDT(Q)/CBS.

In Table 3.1, an incremented focal point table is shown. As it can be seen as the degree of correlation increases, the energy converges to the CBS limit.

After CBS energies are obtained, several corrections are added to get even more exact energies by approaching chemical accuracy.

	RHF	+ δ MP2	+ δ CCSD	+ δ CCSD(T)	+ δ CCSDT	+ δ CCSDT(Q)	NET
aug-cc-pV(D+d)Z	+19.29	-12.29	+2.20	-1.76	-0.22	-0.15	[+7.06]
aug-cc-pV(T+d)Z	+20.54	-13.04	+2.23	-2.08	[-0.22]	[-0.15]	[+7.29]
aug-cc-pV(Q+d)Z	+20.32	-13.24	+2.15	-2.15	[-0.22]	[-0.15]	[+6.71]
aug-cc-pV(5+d)Z	+20.33	[-13.31]	[+2.13]	[-2.18]	[-0.22]	[-0.15]	[+6.60]
CBS LIMIT	[+20.35]	[-13.39]	[+2.10]	[-2.21]	[-0.22]	[-0.15]	[+6.48]

TABLE 3.1: Incremented focal point table.

1. Diagonal Born-Oppenheimer corrections (Δ_{DBOC}) [180, 181] are computed at the RHF/aug-cc-pV(T+d)Z to account for contributions beyond the Born-Oppenheimer approximation by:

$$\Delta_{\text{DBOC}} = \langle \Psi_e(\mathbf{r}; \mathbf{R}) | \hat{T}_n | \Psi_e(\mathbf{r}; \mathbf{R}) \rangle \quad (3.3)$$

In this correction $\hat{T}_n$ corresponds to the nuclear kinetic operator and $\Psi_e(\mathbf{r}; \mathbf{R})$ is the electronic wave function with parametric dependence on nuclear coordinates.

2. To quantify contributions coming from inner electrons, a frozen core correction (Δ_{core}) was computed.

$$\Delta_{\text{core}} = E_{\text{AE-CCSD(T)}}^{\text{cc-pCV(T+d)Z}} - E_{\text{FC-CCSD(T)}}^{\text{cc-pCV(T+d)Z}} \quad (3.4)$$

In Eq. 3.4, AE indicates that all-electrons are including in the correlation procedure, whereas FC stands for the frozen-core approximation.

3. Scalar relativistic effects were included at the AE-RCCSD(T)/DPT2 theory by including the Darwin term and one-electron and two-electron mass-velocity terms [182, 183].

$$\Delta_{\text{rel}} = \Delta E_{\text{AE-CCSD(T)/DPT2}} - \Delta E_{\text{AE-CCSD(T)}} \quad (3.5)$$

4. To get both activation and reaction enthalpies at zero Kelvin, zero point vibrational energies were computed using the harmonic oscillator approximation at the RCCSD(T)/*aug*-cc-pV(T+d)Z level of theory. Enthalpies are then computed as:

$$\Delta H_{0K} = \Delta E_{\text{CBS}} + \Delta_{\text{DBOC}} + \Delta_{\text{core}} + \Delta_{\text{rel}} + \Delta_{\text{ZPVE}} \quad (3.6)$$

$$\Delta H_{0K} = \Delta E_{\text{CBS}} + \sum \delta\Delta \quad (3.7)$$

In this last equation, the term $\sum \delta\Delta$ collects all correction terms. All energetic computations were done in CFOUR v2.0.

The minimum energy pathway was followed using the intrinsic reaction coordinate (IRC) method as implemented in the Gaussian16 software package using restricted second-order Møller Plesset perturbation theory RMP2/*aug*-cc-pVTZ. A step size of 0.1 Bohr amu^{1/2} was used for IRC computations. Then, single point computations at the CCSD(T)/cc-pVTZ level of theory were performed on each structure on the IRC using Psi4. Symmetry-adapted perturbation theory (SAPT) calculations were performed at the SAPT2+3(CCD)-CT/cc-pVTZ level of theory.

3.3 Results and Discussion

3.3.1 The Mechanism of H_2 Activation by the $[K\{Al(NON)\}]_2$ Aluminyll Anions: Do the Potassium Atoms Play any Catalytic Role?

This section aims to shed light on the different mechanisms of H_2 activation by dimeric and monomeric aluminyll anions. Structures for the H_2 activation were obtained using density functional theory. However, energetic results are reported through single point computations at the DLPNO-CCSD(T)/def2-TZVP on the previously obtained structures at the M06-2X/def2-SVP.

Computation of complex **IV** and its monomer derivative was done using a simpler molecular structure: ^tBu and ^iPr groups were exchanged by methyl substituents giving place to dimeric complex **D** and monomeric complex **M** in Figure 3.2. Molecular orbital investigations (Figure 3.3) showed that the HOMO is mainly centered in the Al lone pairs, exhibiting a change of phase in the dimeric complex **D**. The HOMO energy was found to be -4.9 eV and 1.7 eV for complexes **D** and **M**, respectively ¹. The HOMO-LUMO gap for complexes **D** and **M** is 5 eV and 1.5 eV, respectively, revealing a diminished stability for the monomeric catalyst. Noncovalent interactions (NCI, Figure 3.2) show that the larger stabilization in complex **D** is due to enhanced attractive CH/CH van der Waals interactions. Interestingly, stable formation of the dimeric form is due to attractive $Al^- \cdots K^+$ coulombic interactions but also through cation $\cdots \pi$ interactions between K^+ and the aryl moieties (Figure 3.2).

¹The value of -4.9 eV is comparable with the -4.7 eV obtained in ref. [157]

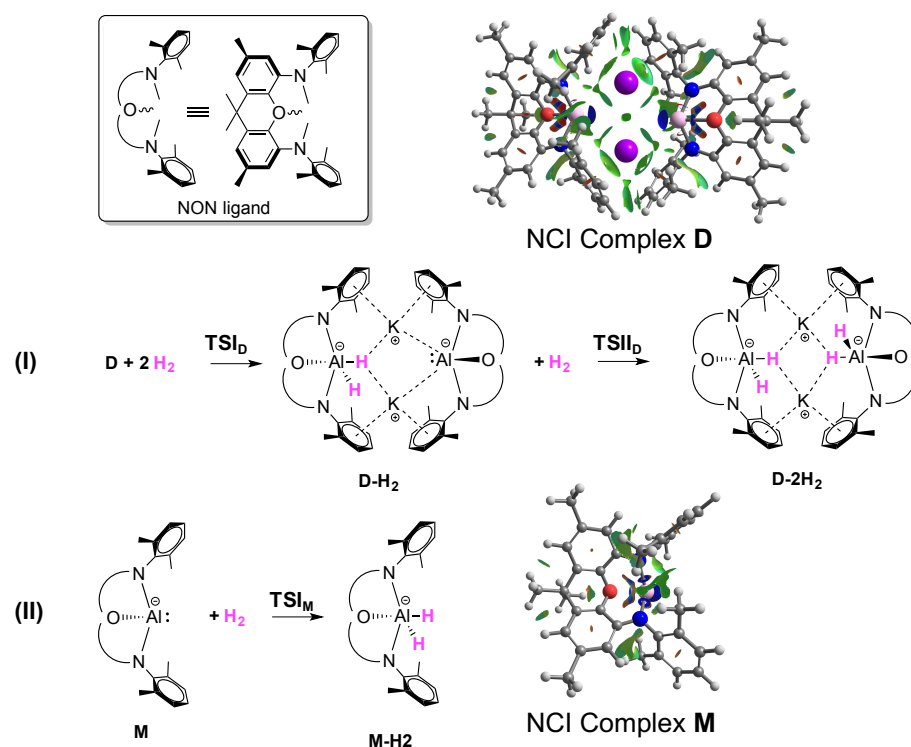


FIGURE 3.2: Reaction pathways for complexes **D** and **M** toward activation of H_2 . Noncovalent interaction (NCI) surfaces for complexes **D** and **M**.

The main stabilizing contributions of a simple $K^+ \cdots \text{aryl}$ interaction are found to be electrostatics ($-14.5 \text{ kcal mol}^{-1}$) and induction ($-10.2 \text{ kcal mol}^{-1}$), with a minor contribution coming from dispersion ($-3.3 \text{ kcal mol}^{-1}$) [184, 185]. Polarization effects predominates the induction term ($-10.1 \text{ kcal mol}^{-1}$), while charge transfer is almost negligible ($0.1 \text{ kcal mol}^{-1}$). On the other hand, for **M**, NCI reveals stabilizing CH/CH interactions along with the xanthene-derived ligand.

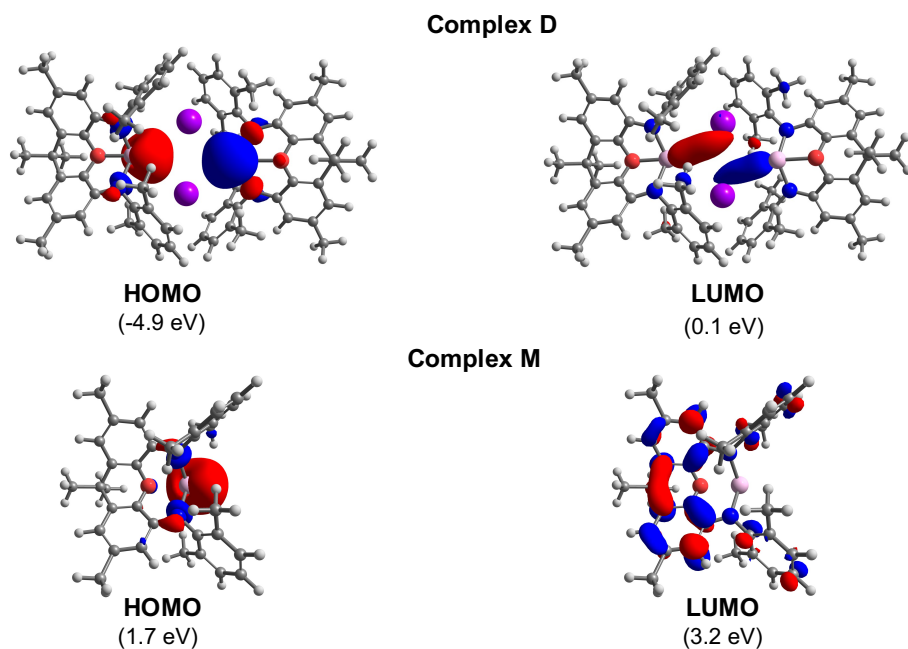


FIGURE 3.3: Isosurfaces and energies of the frontier molecular orbitals HOMO and LUMO for complexes **D** and **M**

In Figure 3.4, the energy profile for both monomeric and dimeric catalyst is shown. The activation of a single H_2 molecule takes place in a one-step mechanism. Although the process is carried out in one kinetic step, the formation of the two Al–H bonds is asynchronous, and different stages appear along the reaction coordinate: (1) polarization of H_2 molecule into $H^+ \cdots H^-$, (2) formation of a first Al–H bond, and (3) formation of the second Al–H bond [156].

For complex **M**, an almost isoenergetic reactant complex, $M+H_2$, lying below the separated reactants is formed with a $\Delta E = -0.8 \text{ kcal mol}^{-1}$. This low stabilization energy is due to the rather low polarizability of hydrogen, and the lack of stabilizing long-range noncovalent interactions. The activation energy of $33.9 \text{ kcal mol}^{-1}$ is obtained, which is characterized by a three-membered transition state (TS), TSI_M . As H_2 approaches the lone pair on the aluminum atom, it polarizes into $H^+ \cdots H^-$. At TSI_M the bond distances (Mayer bond orders) are Al–H', Al–H, and H–H are 1.63 (0.72),

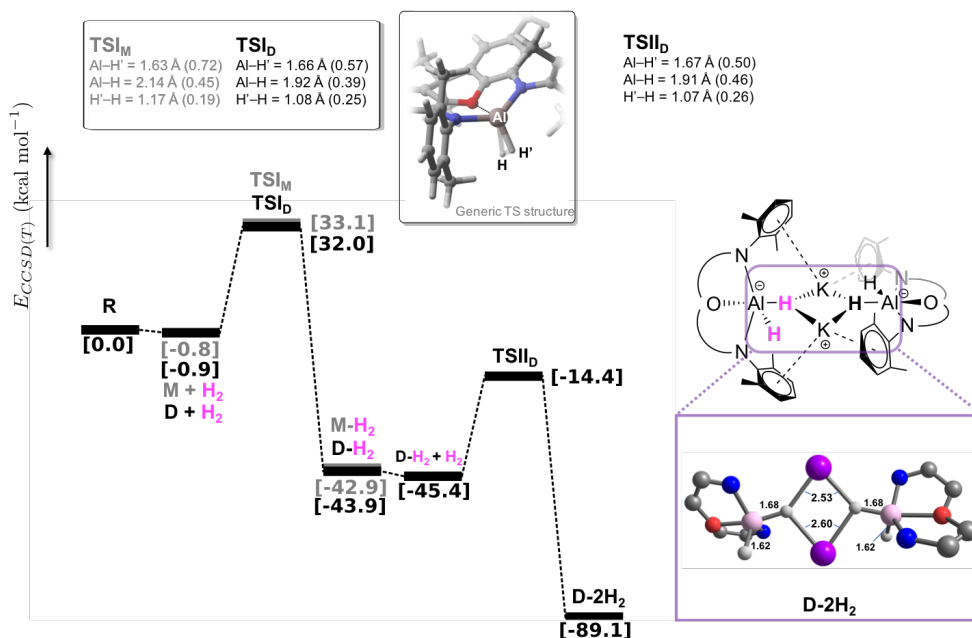


FIGURE 3.4: Energy profile for the activation of H_2 by catalysts **D** and **M**. Bond distances and Mayer bond orders (in parenthesis) are reported for transition states. Energies were computed at the DLPNO-CCSD(T)/def2-TZVP and reported in kcal mol^{-1} .

2.14 (0.45) and 1.17 (0.19) Å, respectively. The H' hydrogen atom is the one that first binds aluminum. As can be observed, at the TS structure, the Al-H bond formation is highly asynchronous. The reaction energy using the anionic monomeric catalyst to form the aluminate **M-H₂** was found to be very exothermic with $-42.9 \text{ kcal mol}^{-1}$.

As mentioned before, the anionic dimeric form is stabilized by both electrostatic ($\text{Al}^- \cdots \text{K}^+$) and cation $\cdots \pi$ ($\text{K}^+ \cdots \text{aryl groups}$) interactions. To study the effect of these interactions in the activation of H_2 and a possible catalytic effect of the potassium atoms, the successive activation of two H_2 molecules was studied. Catalyst **D** forms a reactive complex with H_2 , which lies very close in energy to the one found for the anionic monomeric catalyst ($-0.9 \text{ kcal mol}^{-1}$). Interestingly, the activation energy of $33.0 \text{ kcal mol}^{-1}$ was observed, which is roughly the same as the one obtained with the monomeric complex. Even, the reaction energy is just 1 kcal mol^{-1} more

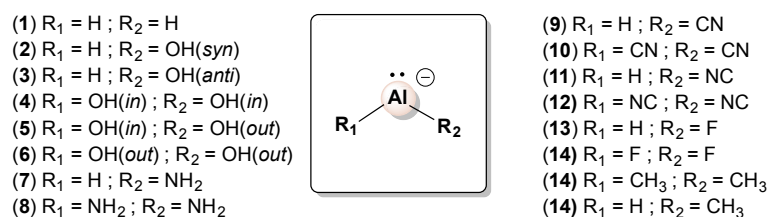
exothermic. This tiny stabilization is due to a $K \cdots H \cdots$ interaction between one of the hydrogens ($-0.54|e|$) and the two potassium atoms ($\sim 0.86|e|$) with distances ~ 2.5 Å. As it can be observed from the bond distances and Mayer bond orders for both **TSI_M** and **TSI_D** in Figure 3.11, a late TS is found for the dimeric catalyst. From the activation energies obtained for the **M** and **D**, potassium atoms do not play a catalytic effect on the dimeric catalyst.

Activation of a second H_2 molecule by complex **D-H2** can also take place. A reactant complex lying $1.5 \text{ kcal mol}^{-1}$ below the **D-H2** product was found. An activation energy of $31.0 \text{ kcal mol}^{-1}$ through **TSII_D** was obtained, which reveals the almost innocent behavior of the potassium cations toward catalysts in this system. However, it may be possible that having a positively charged potassium and a negatively charged aluminum atom, a ionic FLP-like reaction can be conceived. Efforts are put forward toward this reaction channel, and it is under active investigation. On the other hand, the reaction energy of $-89.1 \text{ kcal mol}^{-1}$ prevents the usage of this complex as a hydrogen storage candidate. In conclusion, regarding the individual activation and reaction energies, the activation of the two H_2 molecules are equivalent and completely disengaged. However, we believe that a synchronic activation of two hydrogen molecules may take place through a dynamically concerted reaction pathway.

3.3.2 Substituent Effect in the Activation of H_2 by Simple Aluminyll Anions

In this section, geometry, electronic structure, and the performance of structurally simple aluminyll anions toward the activation of H_2 are studied. In particular, the substituent effect will be analyzed in symmetrically and unsymmetrically substituted aluminyll anions shown in Figure 3.5.

FIGURE 3.5: Substituted aluminyll anions studied in this work.



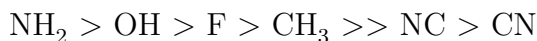
With the recent spectroscopic observation of a simple amino carbene ($H\ddot{C}NH_2$) in argon matrix [186], it is possible that more interest will be devoted to these simple systems, which represent an outstanding opportunity for collaboration between theory and experiment. Here we report geometries at the CCSD(T)/cc-pV(T+d)Z level of theory together with activation and reaction energies for the process of H_2 activation at the CCSD(T) extrapolated to the complete basis set (CBS) limit. Correlation consistent basis sets of Dunning were employed, which increase proportionally in size to accurately converge to the CBS. Several corrections, including core, diagonal Born-Oppenheimer, zero-point vibrational energy, and relativistic corrections, are able to give energetics below the sub-chemical accuracy ($< 1 \text{ kcal mol}^{-1}$).

Because aluminyll anions mimic the valence electronic structure of carbenes, the potential to have a low-lying triplet state competing with a single one exists. However, for the dihydride aluminyll anion, AlH_2^- , the singlet electronic state lies lower in energy by roughly 14 kcal mol^{-1} , computed at the

CCSD(T)/aug-cc-pV(Q+d)Z level of theory. Because of this energetic difference and the number of structures considered here, we have chosen to focus our efforts only in the lowest energy singlet state. Future work may consider the triplet geometries of these molecules for comparison purposes.

3.3.2.1 Orbital Interactions

Low valent main group compounds are extremely prone to polymerization and disproportion reactions due to its high reactivity, together with their diminished kinetic persistence and poor thermodynamic stability in ambient conditions. We focused our attention on the orbital interactions that would dominate the relative orbital stabilization by using non-bulky substituents. In particular, the ability to donate electron density of the substituents toward the p -orbital in aluminum, together with possible back-donation effects from the aluminum atom to the substituents, is taken into account. This ability to donate electron density into the empty p -orbital is reported using second-order perturbation energy ($E^{(2)}$) from NBOs between the substituent and empty p -orbital on aluminum. These values are reported in Table 3.2. The larger the $E^{(2)}$ value, the larger the donation. From the $E_{aluminyl}^{(2)}$ energies in Table 3.2, the p -orbital donating ability for each substituent can be ranked as such:



It should be noted that there is a great separation in the energies among the substituents NH_2 , OH , F , and CH_3 with the C, N-containing substituents. We would refer NH_2 , OH , and F groups as strongly donating groups while NC and CN are weakly donating, but good acceptor substituents. The CH_3 substituent was found to be medium strength donating group, but $E^{(2)}$ reported that the methyl group is a strong acceptor functional group through

back-donation toward the $\sigma^*(\text{C-H})$ bond. On the other hand, no $E^{(2)}$ donation was observed from nitrogen to aluminum in system **7**. This fact is due to the electron pair on nitrogen establishes a strong resonance with the p -orbital on the Al atom, and therefore no $E^{(2)}$ energy is observed.

Another relevant orbital donation we have found to be present in this low valent aluminum forms corresponds to the donation from the diffuse 3s orbital of the aluminum back into the anti-bonding orbitals in the substituent moieties. In Figure 3.6, selected NBO interactions are shown for substituent $\rightarrow$ Al interactions and back-donation effects. For system **3**, the oxygen's lone pair donates electron density onto the empty p -orbital on aluminum, with a stabilization energy of 14.21 kcal mol⁻¹. In this system, small back-donation effects from aluminum onto the substituent were observed with a negligible stabilization energy of 0.87 kcal mol⁻¹. On the other hand, for the dihydroxy species, three stereoisomers were found from the different directions hydrogens can be pointing. As can be seen from Table 3.2, $E_{\text{aluminyl}}^{(2)}$ energies are very close for systems **4**, **5** and **6**. In Figure 3.6, interactions for systems **4** and **5** are shown as representatives. As it may be seen, a small difference of 1 kcal mol⁻¹ for the donation from the lone pair at the oxygen atom onto aluminum is observed for systems **4** and **5**. Conversely, a noticeable difference appears for the back-donation effect. For system **4**, the spatial orientation of hydroxy groups favors a more effective Al $\rightarrow$ $\sigma^*(\text{O-H})$ back-donation over system **6**.

System **7** represents an extreme case of study, in which no substituent $\rightarrow$ Al donation was observed. However, back-donation from Al to $\sigma^*(\text{N-H})$ bond orbital is present, with stabilization energy of 3.92 kcal mol⁻¹. Opposite to system **7**, a LP(N) $\rightarrow$ LP*(Al) donation in the diamino aluminyl anion is observed, with $E_{\text{aluminyl}}^{(2)} = 15.61$ kcal mol⁻¹. In this system, the electron density donated from the nitrogen atom to the empty p -orbital orbital in aluminum is back donated towards the $\sigma^*(\text{N-H})$ bonds, with relatively high stabilization

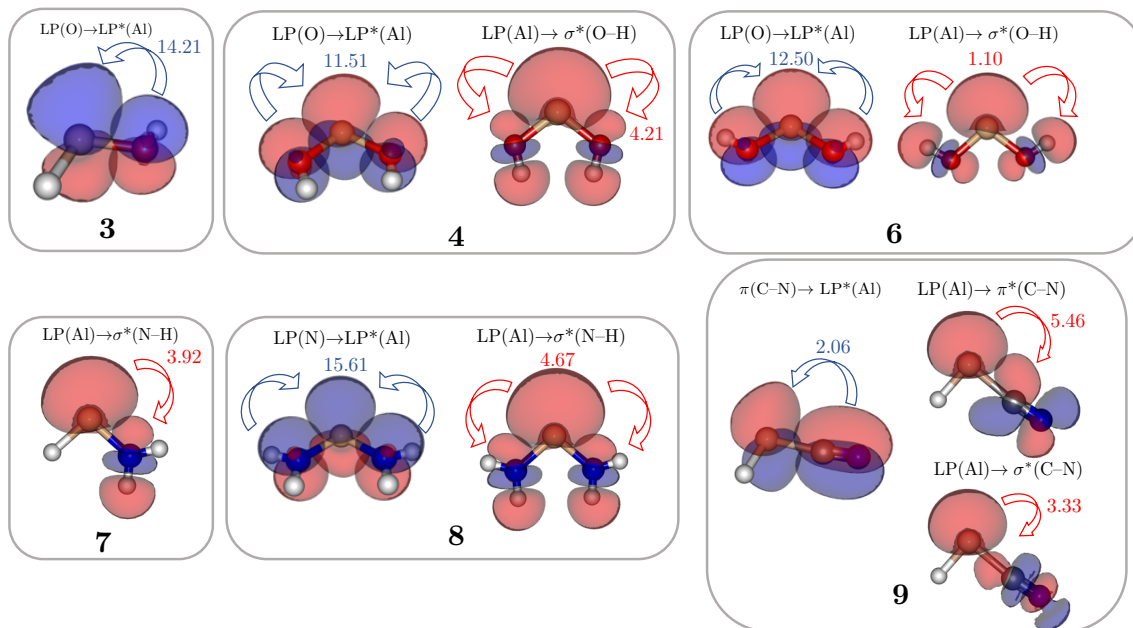
energy of 4.67 kcal mol⁻¹ (compared among the strong-donating substituent family). Interestingly, back-donation was only observed from aluminum to N–H bonds that are in the same direction concerning the lone pair in Al, as it is shown in Figure 3.6.

TABLE 3.2: $E^{(2)}$ energies from the natural bond orbital analysis. $E_{aluminyll}^{(2)}$ is the substituent→Al donation while $E_{BD}^{(2)}$ accounts for back-donation effects. For systems **9-12**, $E_{BD}^{(2)}$ energies for LP(Al)→ π^* (C,N bond) (left) and LP(Al)→ σ^* (C,N bond) (right) are reported.

Species	R ₁	R ₂	$E_{aluminyll}^{(2)}$	$E_{BD}^{(2)}$
2	H	OH(<i>syn</i>)	13.93	1.64
3	H	OH(<i>anti</i>)	14.21	0.87
4	OH(<i>in</i>)	OH(<i>in</i>)	11.51	4.21
5	OH(<i>in</i>)	OH(<i>out</i>)	11.64 (OH(<i>in</i>)) 12.43 (OH(<i>out</i>))	1.19 (OH(<i>in</i>)) 2.69 (OH(<i>out</i>))
6	OH(<i>out</i>)	OH(<i>out</i>)	12.50	1.10
7	H	NH ₂	...	3.92
8	NH ₂	NH ₂	15.61	4.67
9	H	CN	2.06	5.46 / 3.33
10	CN	CN	2.06	8.25 / 3.50
11	H	NC	3.26	3.15 / 3.10
12	NC	NC	2.93	3.73 / 3.02
13	H	F	10.54	...
14	F	F	9.19	...
15	H	CH ₃	6.66	13.42
16	CH ₃	CH ₃	9.29	31.50

For the weakly donating (CN and NC) substituents, $E_{aluminyll}^{(2)}$ values are the lowest for the series of substituents studied, ranging from 2.06 to 3.26 kcal mol⁻¹. Interestingly, it can be seen that in general, back donation energies, $E_{BD}^{(2)}$, are larger than the $E_{aluminyll}^{(2)}$. The electron-withdrawing nature of the

FIGURE 3.6: Selected NBO interactions for systems **3**, **4**, **6**, **7**, **8**, and **9**. Substituent $\rightarrow$ Al and back-donation interactions are schematized in blue and red arrows, respectively. Second order energies are reported in kcal mol $^{-1}$.



substituents promotes donation from Al to these substituents. From the NBO results, we have found that two mechanisms rule the donation from LP(Al) to the C, N containing species. In Figure 3.6, system **9** is shown as example. As can be seen, the donation from the π (C-N) bond to aluminum is very low, with 2.06 kcal mol $^{-1}$. Conversely, there are two ways that aluminum donates electron density into the C-N bond. The strongest of these donations is from LP(Al) $\rightarrow$ $\pi^*($ C-N), and the weakest is carried out by LP(Al) $\rightarrow$ $\sigma^*($ C-N). For system **9**, the LP(Al) $\rightarrow$ $\pi^*($ C-N) and LP(Al) $\rightarrow$ $\sigma^*($ C-N) are 5.46 and 3.33 kcal mol $^{-1}$, respectively. Finally, for fluorinated species, it was found that donation from LP(F) $\rightarrow$ LP*(Al) is predominant. However, back-donation was not found in the fluorinated systems, most probably due to the low polarizable nature of fluorine.

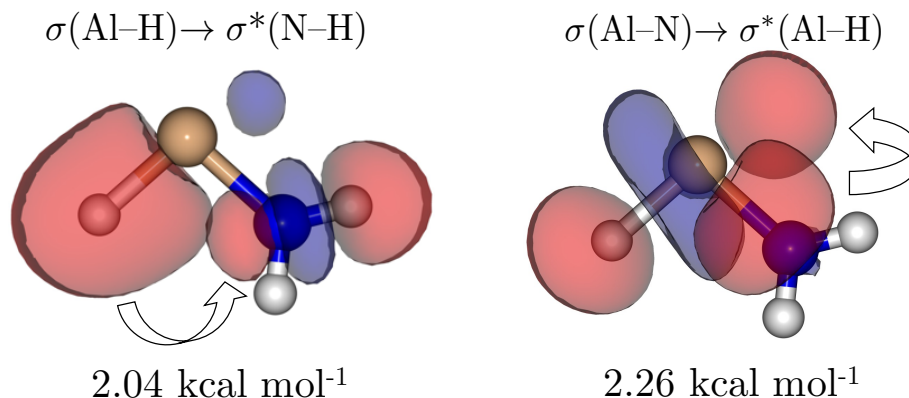
FIGURE 3.7: Mono- and di-substituted aluminyl anions under consideration.

3.3.2.2 Molecular Geometries of Aluminyl Anions

Structures with relevant geometrical parameters for each aluminyl anion species are shown in Figure 3.7. In these systems, differences in the R_1 –Al– R_2 bond angle is of great interest. As mentioned above, it is helpful to divide the group of substituents studied into strongly and weakly donating groups as dictated by the $E_{aluminyl}^{(2)}$ energies. It was found that for the strong donor substituents, the bond order between the substituent and the aluminum increases and therefore causing a bond contraction. An excellent comparison to observe in this trend is the difference in the bond angles for the amino species and the isocyano species.

The R_1 –Al– R_2 bond angle in the monoamino species **7** is 96.0° , which is nearly the same as in the angle found species **1**. According to the NBO results, both the hydrogen and the amino nitrogen in system **7** bear a negative charge. The resulting bond angle is the result of balancing out the repelling negative charge of the nitrogen and hydrogen while maximizing positive interaction with the positive charge on the aluminum center. Furthermore, it was found that stereoelectronic effects help stabilize the rather low angle in species **7** through secondary orbital interactions. From Figure 3.8, it can be seen that two secondary interaction may help to maintain the low N–Al–N angle, in particular, the $\sigma(\text{Al-H}) \rightarrow \sigma^*(\text{N-H})$ interaction ($2.04 \text{ kcal mol}^{-1}$) becomes more favored as the N–Al–N angle decreases reasonably. On the other hand, a $\sigma(\text{Al-N}) \rightarrow \sigma^*(\text{Al-H})$ interaction ($2.26 \text{ kcal mol}^{-1}$) is also favored at the current angle. In summary, the suitable equilibrium between these two secondary interactions at the current structure helps to maintain the rather low N–Al–N bond angle.

FIGURE 3.8: Secondary orbital interactions in systems **7**. $E^{(2)}$ energies are shown below each interaction.



Within the diamino species (**8**), an increase of 3.4 degrees in the N–Al–N angle can be observed, as a consequence of exchange hydrogen for an amino substituent. This steric effect causes the angle to widen. A more subtle effect is also found during NBO analysis. As shown in Figure 3.6, donation and back-donation effect ($E_{\text{aluminum}}^{(2)} = 15.61$ kcal mol⁻¹ and $E_{BD}^{(2)} = 4.67$ kcal mol⁻¹, respectively) are being favored as the N–Al–N increases, causing a more favorable substituent–Al orbital interaction. In conclusion, stereoelectronic effects play a key role in the molecular structure and therefore in the relative stabilization of these species.

Contrasting the latter results with the isocyano derivative, it can be seen that the isocyano species have a smaller inter-substituent bond angle than species **1**. The same forces at work in the amino case are at work here. The first thing to notice is the much longer Al–N bonds present in the isocyano case. This is because there is much less significant donation ($E_{\text{aluminum}}^{(2)}$) from the isocyano compared to the amino group. This means that the bond is weaker and thus elongated.

For the isocyano and cyano groups, we find that the *trans* forms of these

molecules are favored in each case (see structures in Figure 3.7). By adopting the *trans* configuration, systems **10-12** benefit energetically as the lone pair in Al donates electrons into the C–N anti-bonding orbital (σ^* or π^*), which is the most important orbital interaction.

A look at the dihydroxy species will give some interesting insights into other effects present within these species. The *in-in* dihydroxy species (**4**) suffers from steric repulsion between the hydrogens, which are pointed at one another in the plane. This steric repulsion causes the bond angle between the hydroxy substituents to widen, resulting in the most significant bond angle reported among all structures. The widening of the angle, in this case, is completely analogous to the case of species **8**. The *in-out* dihydroxy species has a significantly smaller bond angle than the other two dihydroxy species. This finding can be explained through two observations: first, the oxygen–aluminum bond lengths are mismatched, meaning that the intersubstituent bond angle decreases further than the *in-in* conformer before repulsion effects between the negatively charged oxygens take effect; second, the attractive force between the positively charged “*in*” hydrogen and the negatively charged “*out*” oxygen. This attractive force would pull the two substituents together, decreasing the bond angle between them. Contracted bond lengths due to increased interactions between the lone pair of electrons in oxygen and the anti-bonding lone pair on aluminum strengthen and shorten the Al–O bond. The interaction between the aluminum lone pair that was present in species **8** is not as strong in this molecule [$E_{aluminyll}^{(2)} = 1.41 \text{ kcal mol}^{-1}$]. This causes a smaller bond angle as observed in Figure 3.7.

The fluorine-containing species **13** and **14** are similar in structure to species **1**. The increase in bond angles comparing to species **1** can be attributed almost entirely to steric repulsion between the substituent atoms.

3.3.2.3 H_2 Activation

The study of the activation of H_2 by substituted aluminyll anions is presented. As has been found in the preceding section, the activation of H_2 takes place in one kinetic step but with the highly asynchronous formation of the two Al–H bonds. For the sake of simplicity, only one configuration for each substituent was selected. The reactions were classified as monosubstituted and disubstituted by having one or two equal substituent groups bonded to aluminum. Transition state structures for monosubstituted and disubstituted aluminyll anions are shown in Figure 3.9 and 3.10, respectively.

Activation and reaction energies were computed at the CCSD(T)/CBS level of theory and corrected by relativistic, core, ZPVE, and diagonal Born-Oppenheimer corrections. Therefore, the energies reported corresponding to enthalpies at zero Kelvin (H_{0K}). Energy profiles for the di- and monosubstituted aluminyll anions are shown in Figure 3.11. For the reactions under consideration, it was found that the lowest activation energy is for the AlH_2^- aluminyll anion species (8.17 kcal mol⁻¹), while the highest activation barrier was found for the disubstituted fluorinated aluminyll anion (34.96 kcal mol⁻¹). Moreover, activation enthalpies for the disubstituted anions range from 8.17 kcal mol⁻¹ (AlH_2^-) to 34.96 kcal mol⁻¹ (AlF_2^-). However, $\Delta\Delta H_{0K}^\ddagger$ values for monosubstituted aluminyll anions span only in a ~ 10 kcal mol⁻¹ range, from 10.92 kcal mol⁻¹ ($AlHCH_3^-$) to 19.46 kcal mol⁻¹ ($AlHNH_2^-$). As can be noticed, for each substituent, the activation energy for the H_2 activation is lower when the aluminyll center bears only one substituent beside hydrogen atoms. In particular, the larger decreasing between the mono- and di-substituted aluminyll anions in the activation enthalpy was found for the fluorinated system with a $\Delta\Delta H_{0K}^\ddagger = 16.65$ kcal mol⁻¹, while the lower decreasing was found for the methylated systems with $\Delta\Delta H_{0K}^\ddagger = 3.64$ kcal mol⁻¹.

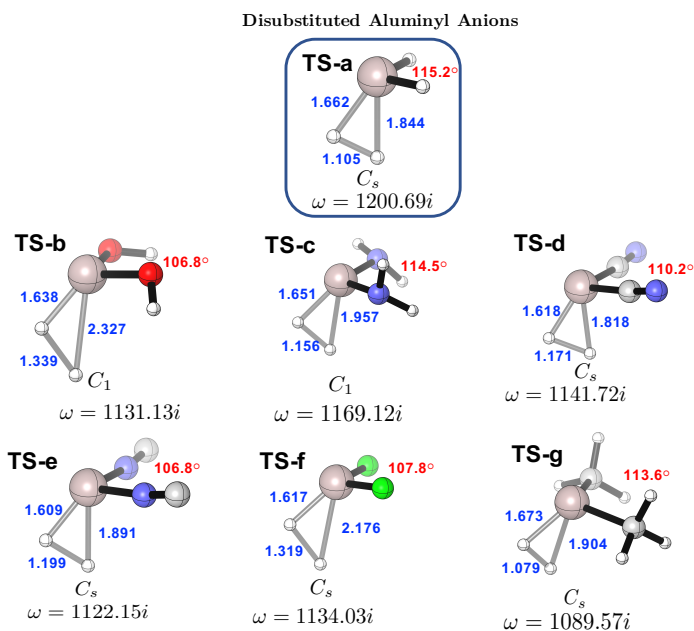


FIGURE 3.9: Transition state structures for symmetrically substituted aluminyll anions. Bond distances (blue) are reported in Å, while the H–Al–R angle is given in degrees (red).

Substituents $-\text{CH}_3$, $-\text{CN}$, and $-\text{NC}$ (in that order) reported the lowest activation enthalpies in both the mono- and di-substituted systems. On the contrary, the substituents $-\text{F}$, $-\text{OH}$, and $-\text{NH}_2$ reported the highest $\Delta H_{0K}^\ddagger$ values. Regarding the inductive electron nature of the substituents $-\text{CH}_3$ and $-\text{F}$, it can be concluded that the donating character of the substituents is preferred, as it was obtained for $-\text{CH}_3$ over $-\text{F}$. An in-depth analysis of the nature of activation energies will be performed using an energy decomposition analysis later in this work.

For reaction enthalpies (ΔH_{0K}°), it was found that, in general, ΔH_{0K}° values are lower for the monosubstituted systems, being the reaction more exothermic. However, this observation is reversed for the methyl substituent, in which more exothermic reaction energy is obtained for the disubstituted system ($-53.58 \text{ kcal mol}^{-1}$) compared to the monosubstituted ($-52.87 \text{ kcal mol}^{-1}$), but with a small energetic difference $|\Delta \Delta H_{0K}^\circ| = 0.72 \text{ kcal mol}^{-1}$.

From the results, it can be concluded that the carbon-coordinated systems

Monosubstituted Aluminyll Anions

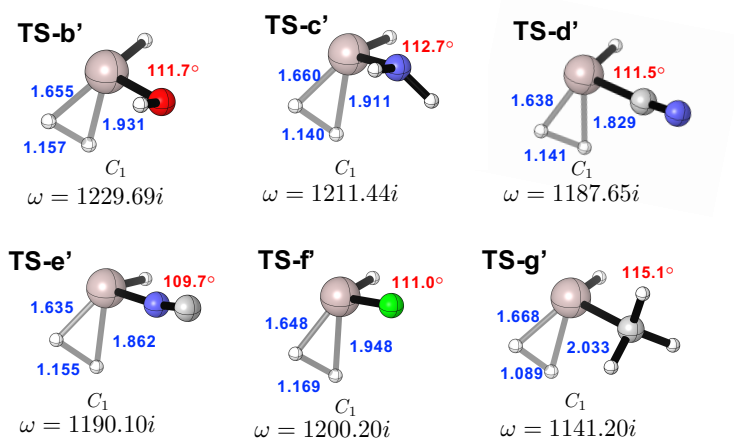


FIGURE 3.10: Transition state structures for unsymmetrically substituted aluminyll anions. Bond distances (blue) are reported in Å, while the H-Al-R angle is given in degrees (red).

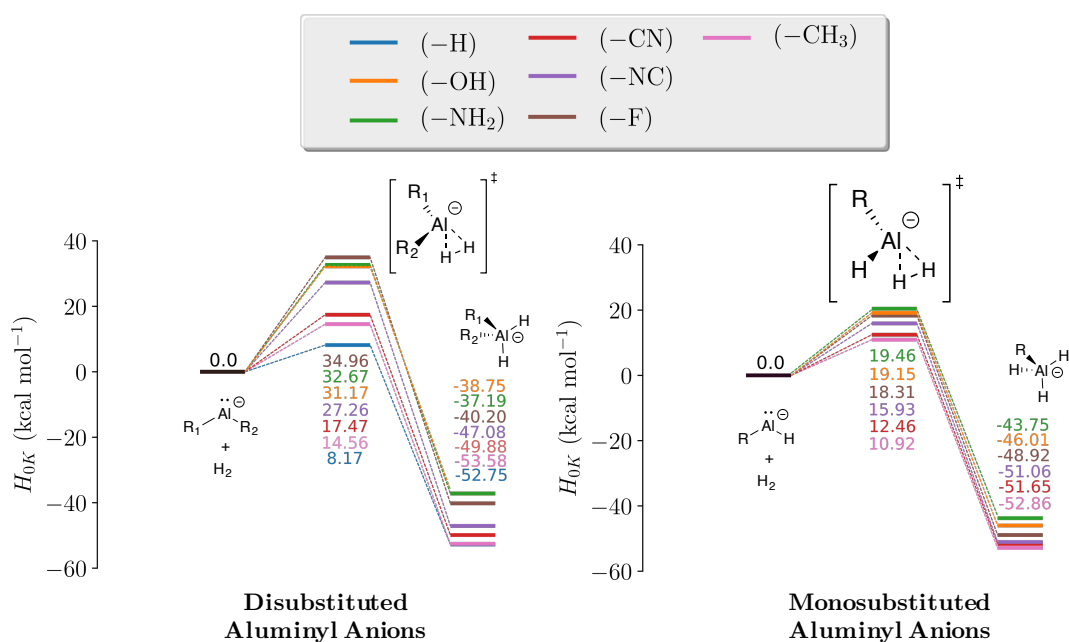


FIGURE 3.11: Energy profile for the activation of H_2 by substituted aluminyll anions. Enthalpies ($\Delta H_{0K} = \Delta E_{\text{CBS}} + \Delta E_{\text{DBOC}} + \Delta E_{\text{core}} + \Delta E_{\text{rel}} + \Delta E_{\text{ZPVE}}$) are reported in kcal mol⁻¹.

(-CH₃ and -CN) perform better regarding activation energies toward the activation of H_2 , but with increased reactivity in the monosubstituted systems. On the other hand, it is worth pointing out that the highly exothermic character of the reactions under study would prevent the usage of aluminyll

anions in H_2 storage applications. In summary, the H_2 activation reaction promotes a favored uptake of the gas but and unfavorable releasing of this gas (for instance, through reductive elimination).

3.3.2.4 Symmetry-Adapted Perturbation Theory Analysis

To study the most important driving forces in the activation of H_2 , a distortion/interaction model based on symmetry-adapted perturbation theory (SAPT) was performed. Most of the distortion/interaction models are computed from the calculation of the distortion energy, which is obtained from the energy of the reacting molecules, not allowing interaction []. The total energy (ΔE) is composed of distortion (ΔE_{dist}) and an interaction (ΔE_{int}) component:

$$\Delta E = \Delta E_{dist} + \Delta E_{int} \quad (3.8)$$

Interestingly, the ΔE_{int} term can be decomposed using Morokuma's energy decomposition analysis. In our approach, the interaction energy is computed free of basis set superposition error and almost exactly using SAPT. From the SAPT computation, the interaction energy can be decomposed in four main physical components as

$$\Delta E_{int} = \Delta E_{elst} + \Delta E_{exch} + \Delta E_{ind} + \Delta E_{disp} \quad (3.9)$$

The terms ΔE_{elst} , ΔE_{exch} , ΔE_{ind} , and ΔE_{disp} are the electrostatic, exchange, induction, and dispersion. The electrostatic term accounts for Coulombic multipole-multipole-type interactions, as an interpretation of charge clouds. The exchange-repulsion contribution corresponds to a repulsive force that comes from the monomer wavefunction overlap, and the fermionic antisymmetry requirements of the dimer wavefunction. Moreover, the induction term includes both polarization from each monomer's response to the other's electric field and charge transfer. Finally, dispersion is an attractive force

resulting from the dynamical correlation between electrons on one monomer with the other's electrons.

Furthermore, SAPT allows to compute charge-transfer energies, and therefore the induction term can be further decomposed into polarization ΔE_{pol} and charge transfer energies ΔE_{CT} ,

$$\Delta E_{ind} = \Delta E_{pol} + \Delta E_{CT} \quad (3.10)$$

It is clear from the distortion/interaction(SAPT) scheme, that this analysis can be easily expanded along the reaction coordinate (adding the dependence of ξ to each term) when subtle physical effects have to be studied along with the reaction coordinate. A similar approach using the reaction force analysis has been proposed recently [187].

To begin with, a study of the activation energies was done using the distortion/interaction(SAPT) model. To carry out a consistent study regarding each substituent. Energies were computed using the TS structures obtained at the CCSD(T)/cc-pV(T+d)Z and the activation energies computed at the CCSDT(Q)/CBS level of theory. Each $\Delta E_i^\ddagger$ component was computed using the isolated reactants as the starting point (possible reactant complexes were not considered in this study). Using the methodology described above, the partition of activation energies in both distortion and interaction components, together with the study of the main physical components, is shown in Figure 3.12. Results in this analysis are shown in increasing order dictated by the activation energies.

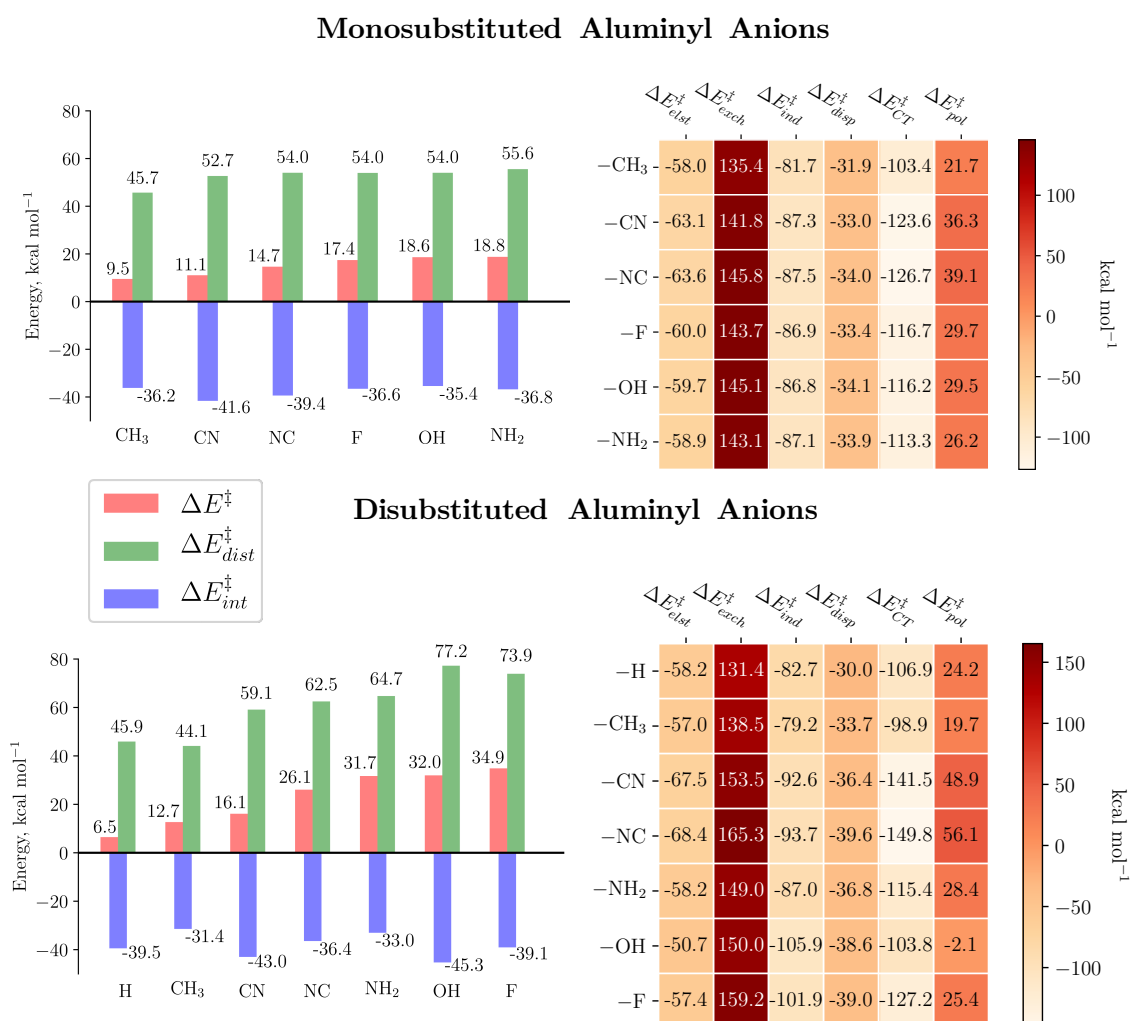
In the left-side of Figure 3.12, the activation energy together with the distortion and interaction components are shown in red, green, and blue, respectively. From the results, it can be seen that the most substantial distortion and interaction energies were found for the dihydroxy aluminyll anion, 77.2

kcal mol⁻¹, and -45.3 kcal mol⁻¹, respectively. It is worth noticing that the current distortion/interaction(SAPT) procedure does not discriminate what is the source of the distortion component is, it can be either (both) the aluminyll anion or (and) the H_2 molecule². From the bar plots in the left-side of Figure 3.12, it can be seen that the distortion component tends to increase as the activation energy does. Inspections on the geometrical parameters' change have shown that the R_1-Al-R_2 angle changes the most for all structures. Therefore, all distortion components have in common the widening of the already cited angle, from the transition from a sp^2 Al center to a sp^3 hybridized Al atom.

As it can be observed for the methylated aluminum anions, the distortion component remains almost the same, but a more stabilizing interaction energy allows the decreasing of the activation energy for the $AlHCH_3$ system. On the other hand, the electron-withdrawing nature of the fluoro substituents has completely the opposite effect. First, the interaction energy remains almost similar for the fluoro- and difluoro-aluminyll anions (-36.6 kcal mol⁻¹ and -39.9 kcal mol⁻¹, respectively). However, the distortion component changes considerably from 54.0 kcal mol⁻¹ to 73.9 kcal mol⁻¹ for the mono- and di-substituted aluminyll anions. The C,N-containing substituents, -CN and -NC, showed intermediate $\Delta E^\ddagger$ values in the series studied. For the mono- and di-ciano aluminyll anions, both distortion, and interaction were found to be lower for the monociano aluminyll species. However, these findings are not the same regarding the isocyano derivatives. It was found that an increased interaction promotes a lowering in the activation energy for the mono-isocyano system. However, the increase of the activation energy for the diisocyano derivative is due to a higher distortion of both aluminyll anion and H_2 molecule.

²This fact corresponds to a disadvantage of other related EDA methods, in which the source of the distortion can be known.

FIGURE 3.12: Analysis of activation energies using the distortion/interaction(SAPT) procedure for mono- and di-substituted aluminyll anions.



For the amino and hydroxy substituents, the high distortion energies observed especially for the disubstituted systems, become the main factor for the high observed activation energies. A large percentage of the distortion energy comes from the torsion of the $-NH_2$ and $-OH$ substituents out-of-planarity, in both mono- and di-substituted aluminyll anions, which is carried out from the reactants to the TSs (see TS structures in Figure 3.9)

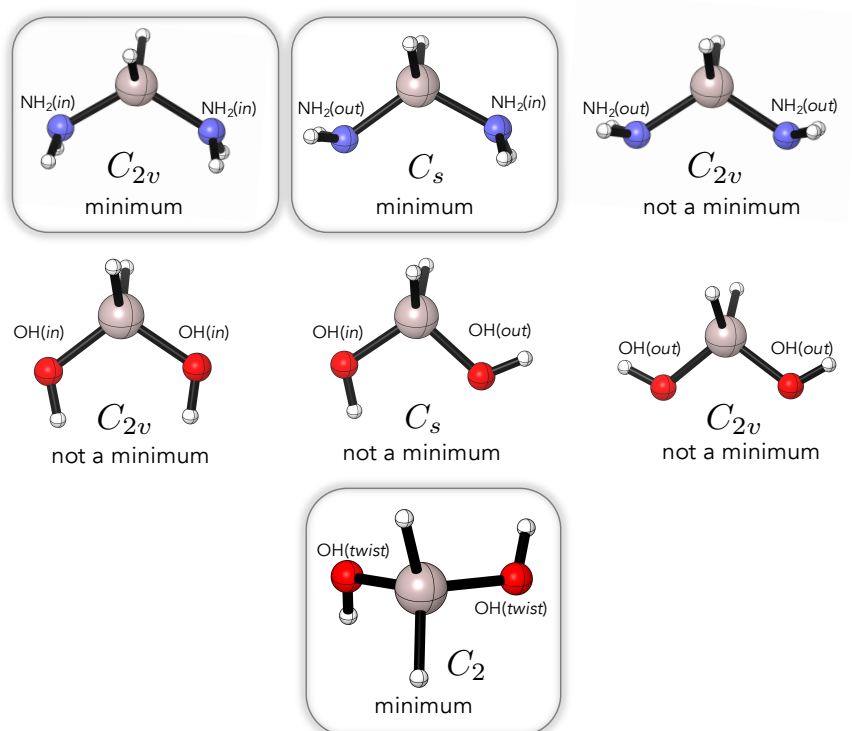
The full characterization of the interaction energy through SAPT is shown

at the right-hand side of Figure 3.12. Above-mentioned energies are given in color-code tables in Figure 3.12. From the results, it can be observed that exchange effects are the most destabilizing energies in the activation of H_2 . However, for each substituent, the induction component plays an important stabilizing role in the observed activation energies. As shown in Eq. (3.10), the $\Delta E_{ind}^\ddagger$ term can be decomposed into charge transfer and polarization energies. From the $\Delta E_{CT}^\ddagger$ and $\Delta E_{pol}^\ddagger$ values, it can be concluded that charge transfer effects give the driving force on the H_2 activation mechanism. In general, destabilizing polarization effects were found for all systems. Interestingly, polarization energies were found to be low, due to the fact the negatively charged aluminyll anions easily polarizes the H–H bond. Noticeably, the dihydroxy aluminyll anion showed a stabilizing polarization effect. This stabilizing polarization energy appears since charge transfer is less stabilizing than the induction term. All the rest of the substituents reverses this fact.

3.3.2.5 Structural Analysis of Products of Activation: The $AlH_2R_1R_2$ Species

After the hydrogenation step, species become tetravalent anions analogous to the simplest AlH_4^- . The AlH_4^- species exhibit a perfect tetrahedral geometry with bond angles of 109.57° . Moreover, the structures are inherently different compared with already studied $AlR_1R_2^-$ species. It is because the hybridization of the central aluminum atom has changed from sp^2 to sp^3 . Because there is not an empty p -orbital in the sp^3 tetravalent species, the π donation energy lowering is no longer available. Therefore, this transition has an effect of breaking the amino- and hydroxy- substituents out-of-planarity. The amino species now have a sp^3 hybridized central nitrogen atom. The loss of π donation also has a significant effect on the energies of the amino species which will be discussed later in this work.

FIGURE 3.13: Identification of different amino- and hydroxy-substituted $AlH_2R_1R_2^-$ tetravalent structures.



For the tetravalent structures, there is a contraction of the Al–H bonds compared to the carbenoid derivative. Because the hybridization has changed, we see that the planarity of the diamino and dihydroxy groups has been eliminated (see Figure 3.13). It has distinct effects upon the electronic structure and, therefore, the molecular geometries. Consider for example the di-amino derivative in which three different structures have to be considered. We have maintained the labeling system that was used for the di-hydroxy and di-amino aluminyll anions to avoid confusion. The structures considered here also belong to a given point group as shown in Figure 3.13. When both amino groups are pointed either *in* or *out*, the symmetry of the structure is C_{2v} whereas the *in-out* structure is of C_s symmetry (Figure 3.13). From the three structures considered, the *out-out* structure exhibits an imaginary frequency (first-order saddle point $\nu_{a_2} = 182.3i$), proving that it is not a minimum on the potential energy surface. Analysis of the imaginary frequency shows a symmetry breaking twisting mode. This vibrational mode arises from the fact that the two lone pairs of the amino groups are pointed directly at one another. The *in-in* and the *in-out* conformers do not suffer from this repulsion interaction and so they are found to be minima.

For similar reasons, the di-hydroxy family within the tetravalent species are not minima in any of the symmetric conformations that were minima in the sp^2 hybridized aluminyll anions: *in-in* (second-order saddle point: $\nu_{a_2} = 330.8i$ and $\nu_{b_1} = 160.2i$), *in-out* (first-order saddle point: $\nu_{a''} = 182.7i$), *out-out* (first-order saddle point: $\nu_{a_2} = 218.8i$). All imaginary vibrational modes for the di-hydroxy derivatives include the breaking of the H–O–Al(H₂)–O–H planarity. This symmetry-breaking mode is due to both electrostatic and steric repulsive forces that exist when the hydrogens point toward either each other or toward the other oxygen atom. The hybridization of the central aluminum atom forces the bond angles in these structures to be much tighter. This forces the O–H bonds to be out-of-plane with each other having a twisted C_2 symmetry structure (bottom part in

TABLE 3.3: Geometries for tetravalent $AlH_2R_1R_2^-$ species used in the isodesmic scheme computed at the CCSD(T)/aug-cc-pV(T+d)Z (*tight(d)*) functions on Al level of theory. All bond lengths given in angstrom ($\text{\AA}$) and all bond angles in degrees.

R_1	R_2	R_1-Al-R_2	$H-Al-H$	$r(Al-R_1)$	$r(Al-R_2)$	$r(Al-H)$
H	H	109.5	109.5	1.645	1.645	1.645
H	OH	106.9	107.9	1.637	1.794	1.650
OH(<i>twist</i>)	OH(<i>twist</i>)	111.5	113.5	1.789	1.789	1.639
H	NH ₂	107.4	108.2	1.656	1.887	1.644
NH ₂ (<i>in</i>)	NH ₂ (<i>in</i>)	118.2	117.5	1.888	1.888	1.641
NH ₂ (<i>out</i>)	NH ₂ (<i>in</i>)	115.5	116.2	1.891	1.880	1.646
H	CN	106.5	112.3	1.623	2.043	1.623
CN	CN	105.5	115.6	2.019	2.019	1.605
H	NC	106.5	112.3	1.623	1.927	1.623
NC	NC	104.8	116.1	1.897	1.897	1.603
H	F	108.6	110.3	1.640	1.725	1.640
F	F	108.2	113.0	1.714	1.714	1.360

Figure 3.13).

3.4 Conclusions

In this section, the activation of H_2 by aluminyll anions has been studied. Aluminyll anions are low valent Al(I) having a lone pair of electrons and a negative charge. In particular, we activation of H_2 by NON-derived catalysts and substituted aluminyll anions were taken into account. For the catalysts bearing the xanthene-derived ligand, both the dimeric and monomeric structures were studied. The activation energies for the activation of the H–H bond were found to be quite similar for the dimeric and the monomeric complex. Furthermore, the activation of a second H_2 molecule by the dimeric catalyst has roughly the same activation energy that the capture of the first hydrogen molecule. Therefore, we conclude that the activation of the two H_2 molecules by the dimeric catalyst is disengaged. More interestingly, the potassium atoms do not play a catalytic role in the activation of H_2 . As aluminum is bearing a negative charge and the potassium atoms bear a positive charge, it may be possible that these two centers act cooperatively for the activation of σ –bonds.

Simple substituted aluminyll anions were extensively studied to reveal the substituent effect over geometry, electronic structure, and their performance in activation of H–H bonds. Orbital donations studied using second-order perturbation theory revealed that donation of the substituent toward the empty p-orbital is carried out. This orbital donation allows the amino and hydroxy group to stay in a planar conformation. Interestingly, back-donation effects were found for all the substituents, except for fluorine (probably due to the low polarizability of fluorine). The latter is a central finding since back-donation is a special feature in transition metal catalysts, now also found in low valent main group compounds.

Regarding the activation of H_2 bonds by the substituted aluminyll anions, it was found that the AlH_2^- species obtained the lowest activation energy.

Interestingly, monosubstituted aluminyll species reported lower activation energies than the disubstituted systems. In general, the carbon-coordinated systems, $-CH_3$, and reported low activation energies in both mono- and di-substituted systems. Using a distortion/interaction(SAPT), it was found that distortion energies show the same tendency with activation energies, while charge transfer effects were found to be crucial in the activation energies for H_2 activation by aluminyll anions.

Appendix A

Theoretical Tools

A.1 Symmetry-Adapted Perturbation Theory

Symmetry-adapted perturbation theory (SAPT) [86] provides a robust way to compute noncovalent interaction energies between two fragments/molecules. The interaction energy is determined without computing the total energy of the monomers or dimer. The simplest SAPT approach is called SAPT0, in which a Hartree–Fock (HF) molecular orbital computation on each monomer is done, and then the intermolecular interaction is computed through second-order perturbation theory.

SAPT allows to decompose the interaction energy into key physical components as: electrostatics (*elst*), exchange (*exch*), induction (*ind*) and dispersion (*disp*). The electrostatic term accounts for Coulombic multipole-multipole-type interactions and interpretation of charge clouds. The exchange-repulsion contribution corresponds to a repulsive force that comes from the monomer wavefunction overlap and the fermionic antisymmetry requirements of the dimer wavefunction. Moreover, the induction term includes both polarization from each monomer’s response to the other’s electric field and charge transfer. Finally, the dispersion is an attractive force resulting from the dynamical correlation between electrons on one monomer with the

other's electrons. Many derivations and various degrees of completeness depending on the size of the system have been introduced, where interaction energies comparable with CCSD(T) can be achieved but with similar computational cost [188].

The Hamiltonian operator of the dimer used in SAPT is partitioned into contributions coming from each of the monomers and the interaction

$$\hat{H} = \hat{F}_A + \hat{W}_A + \hat{F}_B + \hat{W}_B + \hat{V} \quad (\text{A.1})$$

$\hat{F}$ represents the Fock operator, $\hat{W}$ the fluctuation potential of each monomer (A or B) and $\hat{V}$ is the interaction potential. The monomer Fock operators ($\hat{F}_A$ and $\hat{F}_B$) are computed from the zeroth-order Hamiltonian, and the interaction energy is evaluated through a perturbative expansion of $\hat{V}$, $\hat{W}_A$ and $\hat{W}_B$. Electrostatic and exchange interactions are computed through first-order in $\hat{V}$ while induction and dispersion appear at second-order in $\hat{V}$.

Although several truncations are developed within the SAPT procedure, SAPT0 constitutes the simplest¹. It is computed as follows

$$E_{\text{SAPT0}} = E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} + E_{\text{disp}}^{(20)} + E_{\text{exch-disp}}^{(20)} + \delta_{\text{HF}}^{(2)} \quad (\text{A.2})$$

Within this notation, the $E^{(vw)}$ term defines the order in V and $W_A + W_B$. The subscript *resp* is an indication that orbital relaxation effects are taken into account. Specifically, the $\delta_{\text{HF}}^{(2)}$ term is obtained from

$$\delta_{\text{HF}}^{(2)} = E_{\text{int}}^{\text{HF}} - (E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)}) \quad (\text{A.3})$$

¹Several SAPT modules are available in the Psi4 software package

and accounts for higher-order induction effects included in the definition of the SAPT terms. These are computed from the HF supermolecular interaction energy E_{int}^{HF} and are only available in dimer-centered basis SAPT computations (usually used as default).

A.2 Energy Profiles and Reaction Force

Potential energy surfaces (PES) are the cornerstone in computational quantum chemistry. They are often studied within the Born-Oppenheimer approximation [189] and represent ways through which chemical species may transform going from one point to another on the potential energy surface. PES are mainly rationalized in terms of differences in energy of the stationary points associated with chemical species involved in a reaction. Due to the high dimensionality of a PES ($3M - 6$ degrees of freedom with M as the number of atoms), the full computation of it becomes unfeasible even for small molecules. The breakthrough in the characterization of a PES is the study of the minimum energy path that connects reactants and products passing through a transition state (TS), giving place to an energy profile as the one shown in Figure B.10(a). Nowadays, computation of a reaction mechanism can be studied by means of the intrinsic reaction coordinate (IRC, ξ) method [190–194]. It allows to obtain an energy profile, suitable to investigate the transition between reactants and products along ξ . Although kinetic and thermodynamic information can be obtained from energy profiles, no further information about the nature of these energies is gained. To gain more insight into the energetics along the reaction, the reaction force $F(\xi)$ has been introduced [195]. The $F(\xi)$ profile is obtained differentiating the potential energy with respect to the reaction coordinate. Most of the time the derivative is performed numerically due to the lack of analytic potential energy functions.

$$F(\xi) = -\frac{dE(\xi)}{d\xi} \quad (\text{A.4})$$

One of the features of the reaction force is that it allows a natural partition of the reaction coordinate into different regions in which different reaction mechanisms might be operating [196, 197, 197–200]. The boundaries of the reaction regions are the critical points of the $F(\xi)$ profile, a minimum at ξ_1 before the transition state and a maximum at ξ_2 after it [201]. Figure B.10

displays a generic energy (a) and reaction force (b) profiles along with the partition of the reaction coordinate. For a single transition state reaction, three reaction region are defined: reactant, transition state and product regions. These reaction regions are defined as follows: reactant region **RR** ($\xi_R \leq \xi < \xi_1$), transition state region **TSR** ($\xi_1 \leq \xi \leq \xi_2$) and product region **PR** ($\xi_2 < \xi \leq \xi_P$) [199, 202]. For reactions taking place through more than one elementary step, more reaction regions have to be considered [203, 204]. In the reactant region structural reordering are emphasized, here most structural deformations and geometrical changes lead to the activated reactants at ξ_1 . The transition state region is mainly dominated by electronic reordering; within this region most bonding changes take place. The reaction force analysis is consistent with a transition state region containing many transient structures instead of a unique transition state, in agreement with the ideas coming from the transition state spectroscopy of Zewail and Polanyi [205, 206]. Within the **TSR** a continuum of transient, unstable structures are formed, and intensive electronic activity –bond breaking and formation processes– is emphasized. After the transition state region, structural relaxations take over, and the reaction force decreases until reaching the zero value at the product’s position, ξ_P . Therefore, the product region is characterized by having a significant contribution coming from structural relaxations that lead to the final reaction products. It is worth to mention that the sign and slope of the reaction force allow rationalizing the driving forces in chemical reactions [202]. Besides, reaction works (W_i) can be defined to quantify the energetic deliverance taking place at any stage of the reaction. Reaction works can be defined within each reaction region through numerical integration of the reaction force [28, 199, 207]:

$$\begin{aligned}
 W_1 &= - \int_{\xi_R}^{\xi_1} F(\xi) \, d\xi > 0 & W_2 &= - \int_{\xi_1}^{\xi_{TS}} F(\xi) \, d\xi > 0 \\
 W_3 &= - \int_{\xi_{TS}}^{\xi_2} F(\xi) \, d\xi < 0 & W_4 &= - \int_{\xi_2}^{\xi_P} F(\xi) \, d\xi < 0.
 \end{aligned}$$

Since W_1 and W_4 are defined in the reactant and product region, respectively, they mostly account for structural rearrangements, whereas W_2 and W_3 (both defined within the TS region) are mostly dominated by electronic effects [197, 201, 207]. In this context, a phenomenological decomposition of activation and reaction energies naturally emerges [197, 207]

$$\Delta E^\ddagger = - \int_{\xi_R}^{\xi_{TS}} F(\xi) d\xi = W_1 + W_2, \quad (\text{A.5})$$

$$\Delta E^\circ = - \int_{\xi_R}^{\xi_P} F(\xi) d\xi = W_1 + W_2 + W_3 + W_4. \quad (\text{A.6})$$

The usefulness of the reaction force analysis in this project will be the characterization of different reaction zones and also the characterization of two new structures besides the R, TS and P: the activated reactant and product located at ξ_1 and ξ_2 , respectively. These new key structures may give relevant information about the reaction mechanism. On the other hand, the definition of the activation and reaction energies in terms of the reaction works will serve as a predicting tool to propose rational improvements on the catalyst with the goal of reducing either (both) structural or (and) electronic rearrangements.

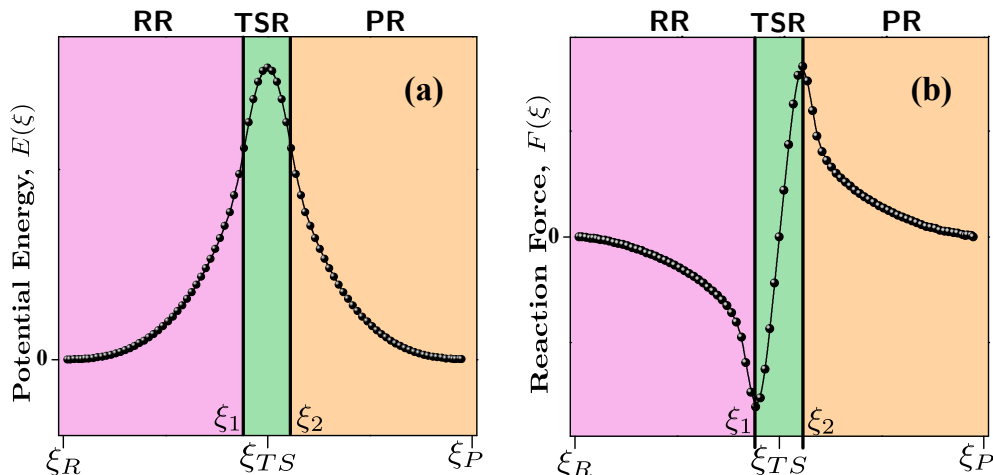


FIGURE A.1: Generic energy (a) and reaction force (b) profiles. Reaction regions are represented in color-code: reactant region (light red), transition state region (green) and product region (orange). The quantities ξ_R , ξ_1 , ξ_{TS} , ξ_2 and ξ_P represent the positions of reactants, activated reactants (force minimum), transition state, activated products (force maximum) and products.

A.3 Reaction Electronic Flux

In density functional theory (DFT) [208], the energy can be written as a function of the total number of electrons of the system N , and a functional of the external potential, $v(\mathbf{r})$: $E \equiv E[N, v(\mathbf{r})]$. Response properties naturally arise by differentiating the energy with respect to the number of electrons and/or the external potential. Differentiating $E[N, v(\mathbf{r})]$ with respect to N give rise to global reactivity properties such as chemical potential and hardness [208, 209]. On the other hand, local reactivity properties are obtained when functional differentiation is performed with respect to the external potential [210]. In particular, μ is conceived as a first order response of the energy with respect to the electron number at constant $v(\mathbf{r})$ (frozen geometry) [208, 210]:

$$\mu = \left(\frac{\partial E[N, v(\mathbf{r})]}{\partial N} \right)_{v(\mathbf{r})} \quad (\text{A.7})$$

Formally in DFT, μ is the Lagrange multiplier that ensures the conservation of the electron number during the energy minimization procedure and, at the same time, it is associated with the Mulliken's definition of electronegativity through $\mu \cong -\chi$ [211]. In this context, μ measures the escaping tendency of

electrons from an equilibrium electronic distribution [208, 210].

Since the energy is not a continuous function with respect to N , differentiation is performed by using the finite difference approximation [208]. It allows to obtain numerical values of μ in terms of the first ionization potential (I_1) and the electron affinity (A_1). Further approximation based on the Koopmans' and Janak's [212] theorems links I_1 and A_1 with the energy of frontier molecular orbitals, HOMO (ϵ_H) and LUMO (ϵ_L) [208–210].

$$\mu = \left(\frac{\partial E[N, v(\mathbf{r})]}{\partial N} \right)_{v(\mathbf{r})} \approx -\frac{1}{2}(I_1 + A_1) \approx \frac{1}{2}(\epsilon_H + \epsilon_L) \quad (\text{A.8})$$

Therefore, by using Eq. (A.8) at each point along ξ it is possible to obtain a chemical potential profile $\mu(\xi)$. It is important to mention that in DFT calculations the second approximation on the right-hand side of Equation A.8 still holds. The latter because in Kohn-Sham calculations it is possible to distinguish occupied and virtual states which are the counterpart of the HOMO and LUMO molecular orbitals in the MO scheme.

To analyze the electronic activity taking place along a reaction coordinate, the reaction electronic flux (REF) has been introduced, [198, 213] it is defined as follows:

$$J(\xi) = -\frac{d\mu(\xi)}{d\xi} \quad (\text{A.9})$$

When $J(\xi) = 0$ no electronic activity besides that of the equilibrium state is observed. Positive values of $J(\xi)$ indicate spontaneous changes in the electronic density that are driven by bond forming or bond strengthening processes. On the contrary, negative values of $J(\xi)$ are evidence of non-spontaneous electronic activity that is driven by bond weakening or breaking processes [28, 198, 199, 203, 213–218].

A.4 Noncovalent Interaction Index

As the ligands that will be used in this study are bulky with the aim of avoiding dimerization among the catalyst units, they may exhibit strong steric and van der Waals interactions that could give rise to different conformations and reactions paths. With the aim of accounting for the noncovalent interactions qualitatively, the noncovalent interaction index (NCI index) will be used[123, 124]. The NCI is based on a two-dimensional plot of the reduced density gradient (s) with respect to $\text{sign}(\lambda_2) \cdot \rho$, where λ_2 is the second density Hessian eigenvalue and

$$s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\Delta\rho|}{\rho^{4/3}}. \quad (\text{A.10})$$

If s is plotted against the electron density ρ solely, noncovalent interactions are revealed by one or more spikes in the low density and low-gradient region. The problem with this is that hydrogen bonds, steric repulsions, and van der Waals are unrecognized since all these interactions appear in the same region. The problem is solved by using the eigenvalues λ_i of the electron-density Hessian matrix ($\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3$). In particular, the sign of λ_2 eigenvalue is used since it can be either negative or positive, allowing to distinguish bonded ($\lambda_2 < 0$) from nonbonded ($\lambda_2 > 0$) interactions. The results extracted from an NCI analysis can be summarized as:

- $\text{sign}(\lambda_2) \cdot \rho < 0$: Hydrogen Bonds
- $\text{sign}(\lambda_2) \cdot \rho \sim 0$: van der Waals interactions
- $\text{sign}(\lambda_2) \cdot \rho > 0$: Steric repulsions

To illustrate the NCI analysis, a 2D plot of s against $\text{sign}(\lambda_2) \cdot \rho$ for a water dimer, methane dimer and bicyclo[2,2,2]octene along with the respective 3D molecular map is shown in color-code in Figure A.2. In this Figure the three kinds of interactions can be seen: the water dimer, the methane dimer, and bicyclo[2,2,2]heptane exhibit hydrogen bond, van der Waals and repulsive interactions, respectively.

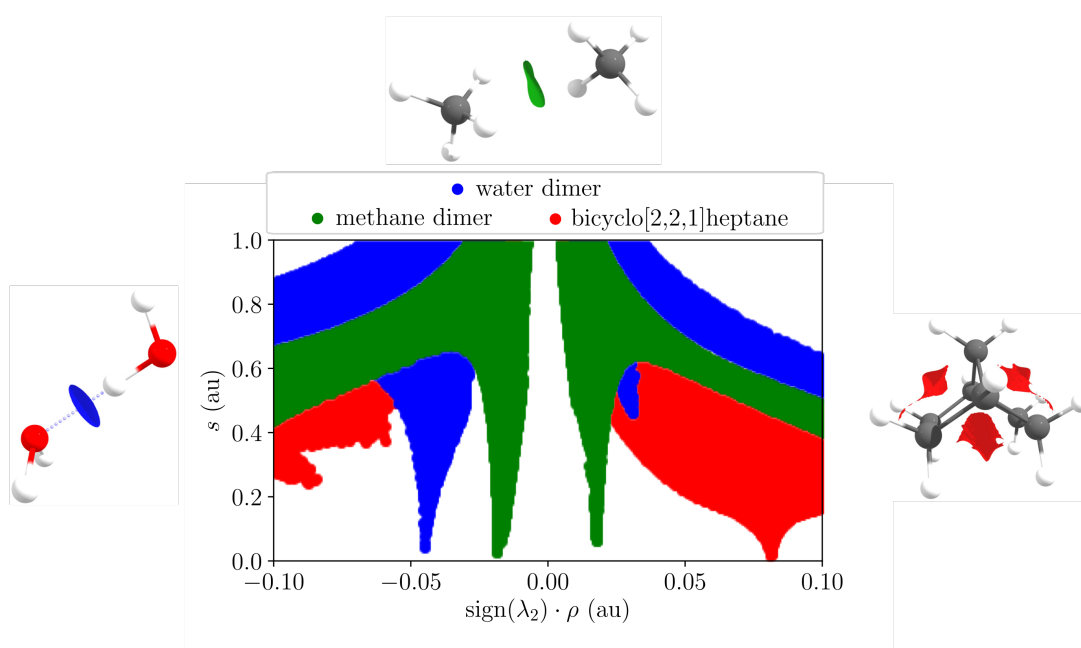


FIGURE A.2: 2D plot of s against $\text{sign}(\lambda_2) \cdot \rho$ along with 3D molecular maps for the three noncovalent interactions (hydrogen bond, van der Waals and repulsive) exemplified by the water dimer, the methane dimer and bicyclo[2,2,2]heptane.

Appendix B

Symmetry-Adapted Reaction Electronic Flux in Cycloaddition Reactions

B.1 General Introduction

Molecular symmetry plays a paramount role in chemistry, ranging from reducing computational efforts in electronic structure methods, to the development of theories that are able to rationalize chemical reactions [219–221]. Most prominently, in 1969, Woodward and Hoffmann (WH) formulated a set of rules aimed to predict the regioselectivity of chemical reactions, in particular for pericyclic reactions. This set of rules are known as the Woodward-Hoffmann rules (WH rules) and are based on the assumption that *orbital symmetry must be conserved throughout the entire chemical reaction*. These rules are explained through the sign of the orbitals involved in the reaction [222, 223]. Later on, Fukui highlighted the relevance of frontier molecular orbital wavefunctions in the explanation of chemical reactions [224, 225] making the fundamental assumption that *a majority of chemical reactions should take place at the position and in the direction of maximum overlapping between the HOMO and the LUMO of the reacting species* [226, 227]. These

two asseverations promoted a breakthrough in the understanding of reaction mechanisms. The quintessential example where WH and Fukui statements are used together to explain a reaction mechanism is found in the cycloaddition reaction between butadiene and ethylene to produce cyclohexene. This reaction was first studied by the pioneering experimental work of O. Diels and K. Alder in 1928 [228] and numerous theoretical studies concerning to the reaction mechanism have been reported since then [227, 229–237]. A one-step and diradical stepwise mechanisms have been proposed, being the former more widely accepted. The concerted pathway proceeds within a σ -plane (C_s symmetry group) and orbital symmetry is conserved throughout the reaction path.

This chapter aims to shed light into the nature of the electronic activity that controls cycloaddition reactions. Furthermore, the breakdown of the Koopmans' and finite differences approximation when computing the chemical potential and its derivatives has been revealed. For this purpose, a whole theoretical framework has been developed called symmetry-adapted reaction electronic flux (SA-REF) [238, 239]. The SA-REF can characterize electronic activity according to a partition in terms of orbital symmetries. Furthermore, the SA-REF is able to distinguish between $\sigma - \pi$, *in-plane* and *out-of-plane* electronic reordering giving a clear picture of the relevance of each event along the reaction coordinate. In this chapter, three Diels-Alder reactions have been studied: **(1)** the emblematic formation of cyclohexene from butadiene and ethylene, together with the formation of o-benzyne via diacetylene plus acetylene, and **(2)** the competing [5, 6] and [6, 6] reaction paths in the cycloaddition reaction between C_{60} and cyclopentadiene.

B.2 Theory

In density functional theory the electronic chemical potential (μ) represents the escaping tendency of electrons from an equilibrium distribution [240, 241], μ is related with the well known classical chemistry concept, the electronegativity χ , through the following relationship [242]:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\mathbf{r})} = -\chi \quad (\text{B.1})$$

Due to the discontinuity of N , the total number of electrons, the chemical potential has to be computed using the finite differences approximation that involves the first ionization potential (IP) and the electron affinity (EA). Moreover, the Koopmans' theorem [243, 244] can be invoked to link μ with the energy of HOMO and LUMO frontier orbitals $\epsilon_H \cong -IP$ and $\epsilon_L \cong -EA$:

$$\mu \approx -\frac{1}{2}(IP + EA) \approx \frac{1}{2}(\epsilon_H + \epsilon_L) \quad (\text{B.2})$$

Changes in the electronic chemical potential along a reaction coordinate can be understood as an electronic activity taking place in a chemical reaction. Therefore, the so-called reaction electronic flux has been defined as the negative derivative of the electronic chemical potential with respect to the reaction coordinate [245–248]:

$$J(\xi) = - \left(\frac{d\mu(\xi)}{d\xi} \right) \quad (\text{B.3})$$

The REF allows to rationalize primary chemical events, such as bond-breaking and bond-forming processes, as well as secondary events, such as bond strengthening and weakening processes. [249–251]. The interpretation of the REF is very straightforward: when $J(\xi) > 0$, it accounts for spontaneous changes in the electron density, which has been shown to be related with bond strengthening or forming process; $J(\xi) < 0$ indicate non-spontaneous

changes in the electronic density which are associated with bond weakening and/or breaking processes [252]. The REF has been able to describe the electronic activity in a wide range of chemical reactions, such as proton transfers [245, 246, 253–255], chemisorption processes [256], S_N2 [247], isomerizations [248], carbocation rearrangements [257], H_2 activation [28, 258], among others.

It is worth to point out that orbital degeneracies may occur along the reaction path by giving rise to degenerated densities, which are problematic when computations of properties are needed along a reaction pathway. To make the picture clearer, let us consider a molecule with point group $\mathcal{G}$ containing irreducible representations Γ_1 and Γ_2 . The irreps Γ_1 and Γ_2 are totally symmetric and unsymmetric with respect to a plane, respectively (ex. A' and A'' in the C_s group). The molecule has six electrons, and two degenerated HOMOs of different symmetry, as shown in Figure B.1. As it can be observed, two electronic configurations (A and B) can be made arranging 6 electrons in 3 orbitals by maintaining the singlet electronic state and having the same energy. Furthermore, in this case, two electronic states could be observed in the degenerate state $^1\Gamma_1$ and $^1\Gamma_2$. As a result, when orbital degeneration appears, it not only gives rise to degenerated densities but it may produce a change in the electronic state (either $^1\Gamma_1$ or $^1\Gamma_2$) as well as a change in symmetry of the molecular wave function. More importantly, as the electron pair may be either in the highest energy Γ_1 or Γ_2 orbitals after the crossing point the symmetry of the HOMO may change giving rise to suddenly energy changes along ξ . Therefore, in these situations, the Koopmans' approximation fails when computing μ at the crossing points. Moreover, when orbital degeneration appears both IP and EA are also prone to give discontinuities. With this in mind chemical potential can not be computed or if it is done they become ill-defined [238, 239].

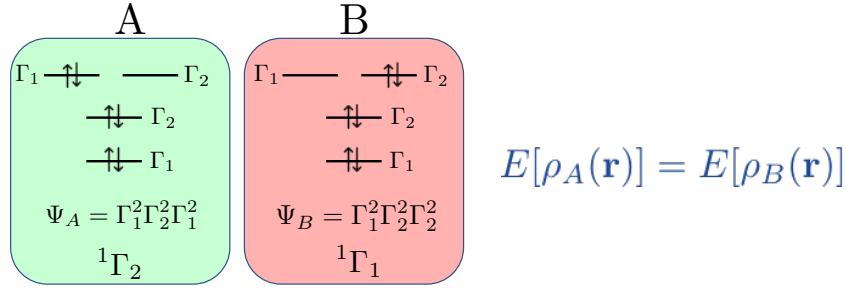


FIGURE B.1: Schematic representation of 2-fold degenerated densities with the corresponding electronic configuration in the singlet state.

A way to circumvent this issue is by computing a SA-CP such that to each irreducible representation $\Gamma_s \in \mathcal{G}$ it corresponds a SA-CP, μ_s , such that:

$$\mu(\xi) = \sum_{s \in \mathcal{G}} \mu_s(\xi) \quad (\text{B.4})$$

Using the chemical potential (CP) expressed in terms of orbital energies (Eq. (B.2)), allows taking advantage of the orbital symmetry constraints along the reaction coordinate. To obtain the SA-CP, molecular symmetry has to be conserved along the reaction path (WH's assumption) [223]. The SA-CP recollects the symmetry of the orbitals that are involved in the reaction according to the irreducible representation to which they belong. Therefore, each HOMO of a given symmetry has associated a respective LUMO of the same symmetry. Thus, the total number of irreducible representations gives the number of occupied and virtual orbitals that will be used to compute the SA-CPs through the orbital approximation as follows:

$$\mu_s = \frac{1}{2n} (\epsilon_s^{occ} + \epsilon_s^{virt}) \quad (\text{B.5})$$

where ϵ_s^{occ} and ϵ_s^{virt} stand for the highest occupied and lowest unoccupied molecular orbital energies of symmetry s , respectively; n is the number of irreducible representations of $\mathcal{G}$.

Applying the negative derivative to Eq. (B.4) with respect to the reaction coordinate, the SA-REF is obtained [238]:

$$J(\xi) = - \left(\frac{d\mu(\xi)}{d\xi} \right) = - \sum_s^{s \in \mathcal{G}} \frac{d\mu_s(\xi)}{d\xi} = \sum_s^{s \in \mathcal{G}} J_s(\xi) \quad (\text{B.6})$$

The total REF is therefore splitted into a sum of individual fluxes associated with different symmetry representations.

B.3 Butadiene plus Ethylene and Diacetylene with Ethylene Reactions

In this section, two-parent Diels Alder reactions taking place through two different symmetric pathways are studied. Reactions under consideration are shown in Figure B.2. Reaction **R1** corresponds to the formation of cyclohexene (C_6H_{10}) from butadiene (C_4H_6) and ethylene (C_2H_4) in a single-step through a C_s symmetry pathway which is conserved all along the reaction coordinate. Reaction **R2** corresponds to the o-benzyne (C_6H_4) formation from diacetylene (C_4H_2) and acetylene (C_2H_2), the reaction is carried out through a C_{2v} symmetry pathway. In this section, the reader will observe that for the case of **R1**, the electronic activity is captured in terms of the symmetry-adapted REF (SA-REF) according to irreducible representations A' and A'' . $J_{A'}(\xi)$ characterizes the electronic activity due to π electronic reordering, while $J_{A''}(\xi)$ encompasses the formation of the new σ bonds. On the more complex o-benzyne formation it displays four SA-REFs associated with each of the irreducible representation of the C_{2v} group. Results show that SA-REFs appear to be very useful for identifying electronic activity that displays a specific symmetry character. In the first reaction, the π electronic activity drives the formation of cyclohexene, whereas, in the second reaction, the in-plane electronic activity drives the formation of o-benzyne.

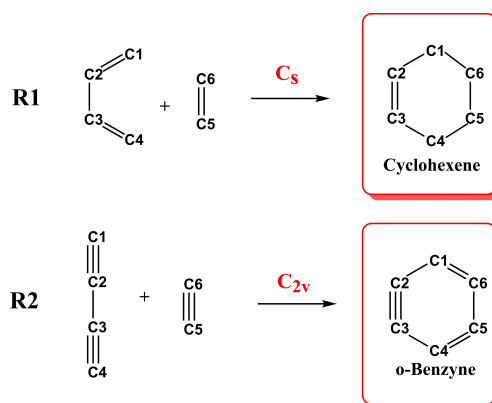


FIGURE B.2: Reactions under study. **R1** proceeds through a C_s reaction path while **R2** is characterized by proceeding in a C_{2v} symmetry regime.

B.3.1 Computational Details

Reaction **R1** system was computed using DFT level of theory. The Becke-3 [259] functional for exchange plus the correlation of Lee-Yang-Parr (LYP) [260] was employed along with the def2-TZVPP basis set [261]. The reason to use B3LYP functional for computing **R1** is because it has been widely used to describe cycloadditions, providing reliable results in both geometry and energy computations [233, 235, 262–264]. On the other hand, **R2** was computed using second-order Møller-Plesset perturbation theory (MP2) along with the correlation consistent cc-pVTZ Dunning’s basis set [265]. This choice is supported by the remarkable geometrical match obtained at the TS structure of **R2** compared to that computed at the $c \sim \text{CCSD(T)-AE/cc-pCVQZ}^1$ level of theory by Xu Zhang and co-workers [266]. Both reactions were computed along the minimum energy path that connects reactant and products through the IRC procedure [267, 268]. The transition states for both reactions were characterized through vibrational analysis, using analytic second derivatives. All quantum computations were performed using Gaussian 09 software package [82]. All profiles and molecular properties were processed using the Kudi Python Library [269].

¹ $E[\text{c} \sim \text{CCSD(T)-AE/cc-pCVQZ}] = E[\text{CCSD(T)/cc-pVTZ}] + E[\text{MP2-AE/cc-pCVQZ}] - E[\text{MP2/cc-pVTZ}]$

B.3.2 Results and Discussions

The breakdown of the finite difference approximation and Koopmans' theorem used to compute $\mu(\xi)$ and the respective $J(\xi)$ is shown in Appendix F. Figure F.2 shows the CPs and REFs for **R1** and **R2** using Koopmans' theorem, while Figures F.3 and F.4 show orbital crossing for both chemical systems and the respective representation of the symmetry-adapted molecular orbitals.

On the other hand, it is essential to mention that finite difference approximation also fails in describing the CP due to the different electronic states that arise at the orbital degeneracy point for the cation and the anion, thus preventing to give an accurate determination of ionization potential and electron affinity. Figures F.5 and F.6 show the CPs and REFs computed using finite difference approximation as well as the computed electron affinities and ionization potential along the reaction path.

B.3.2.1 Energy and Reaction Force Analysis

Energy profiles of both reactions are displayed in Figure B.3, and transition state structures are shown in Figure B.4 in which structural parameters of reactants are given in parenthesis. The reader is referred to Section A.2 for a detailed description of the reaction force approach. Energetic parameters extracted from the energy and reaction force profiles are quoted in Table B.1.

From Table B.1 it can be observed that the activation energy ($\Delta E^\ddagger$) computed for **R1** amounts to 20.7 kcal mol⁻¹, the structural (W_1) and electronic (W_2) reaction works are 15.4 and 5.3 kcal mol⁻¹ that corresponds to 74% and 26% of the activation barrier.

On the other hand, the o-benzyne formation (**R2**) has a barrier height of 28.2 kcal mol⁻¹ calculated at the MP2/cc-pVTZ level of theory. Further, the

Reaction	$\Delta E^\ddagger$	ΔE°	W_1	W_2
R1	20.7	-34.0	15.4	5.3
R2	28.2	-62.1	20.2	8.0

TABLE B.1: Energetic Properties of each reaction. Remember that $\Delta E^\ddagger = W_1 + W_2$. All values in kcal mol⁻¹.

partition of the energy barrier in terms of structural and electronic energies has an associated structural work of 20.2 kcal mol⁻¹ (72%) and electronic energy of 8.0 kcal mol⁻¹ (28%). Note that according to Eq. A.5 the activation energy is composed of W_1 and W_2 , in both reactions it is predominantly structural, thus stressing a similarity between both chemical processes. It is interesting to note that the structural distortion work (W_1) in **R2** is larger than in **R1**. This strain energy is since the distortion in linear diacetylene requires a larger amount of energy than the required to distort butadiene, in order to reach the structure where the electron transfer is initiated. This changes can easily be visualized in **R2-TS** structure shown in Figure B.4. The $\angle 123$ and $\angle 234$ angles involved in the diacetylene's deformation have changed approximately by 38° from the reactant structure, while in butadiene (**R1**) the change amounts to just a few degrees (5.2°). This angular distortion becomes the main factor in the differences in structural energies between both reactions. Besides, it is worth noting that **R2** is much more exoenergetic than **R1**, thus making the reverse process very unlikely to take place.

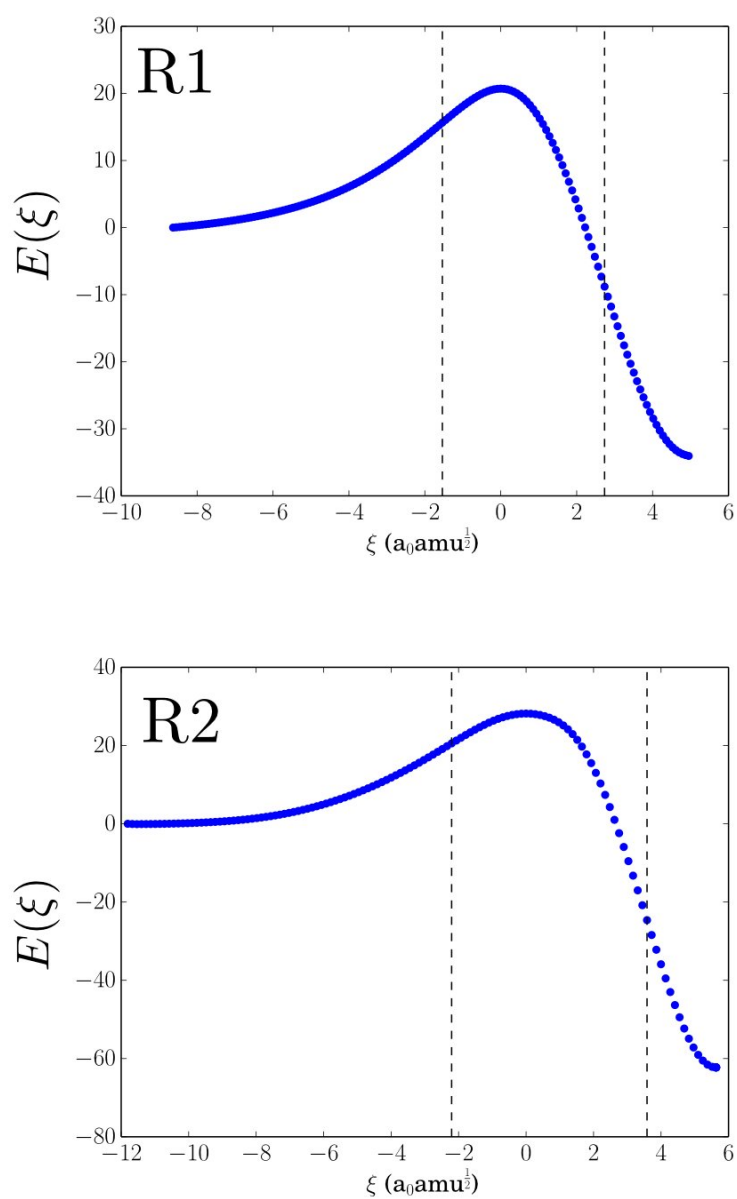


FIGURE B.3: Energy profiles for **R1** and **R2** cycloaddition reactions. Values in kcal mol^{-1} . Vertical dashed lines defines the reaction regions that comes out from the reaction force analysis.

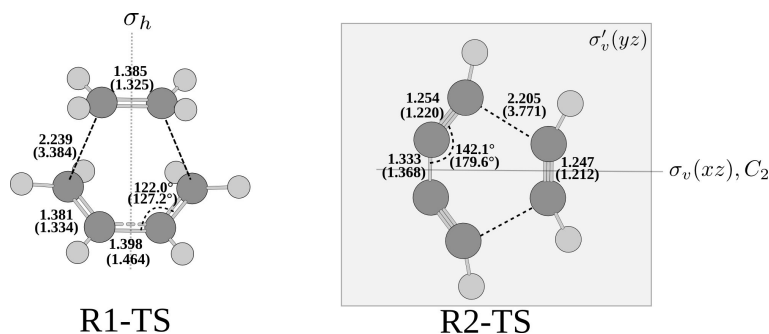


FIGURE B.4: Transition state structures for cycloadditions **R1** and **R2**. Bond distances and angles of the reactant structure for each reaction are given in parenthesis. Bond distances and angles are given in Å and degrees, respectively.

B.3.2.2 Symmetry Adapted Reaction Electronic Flux

(R1) Formation of Cyclohexene

The C_s symmetry group, which is conserved along the entire reaction, allows to define two SA-REFs, $J_{A'}(\xi)$ and $J_{A''}(\xi)$. $J_{A'}(\xi)$ is obtained from the completely symmetric frontier orbitals with respect to the σ_h plane that bisects both molecules (orbitals $13A'$ and $14A'$). On the other hand, $J_{A''}(\xi)$ involves the antisymmetric representation of the frontier molecular orbitals concerning the same molecular plane ($10A''$ and $11A''$). The total REF ($J(\xi)$) is given by $J(\xi) = J_{A'}(\xi) + J_{A''}(\xi)$. Figure B.5 depicts the two atomic orbital interactions of each irreducible representation, A' and A'' respectively. In this reaction, three π -bonds are broken while one π and two σ -bonds are formed; these are the primary events that drive the electronic activity along the reaction coordinate.

In Figure B.6, the total reaction electronic flux ($J(\xi)$) along with its symmetry adapted contributions $J_{A'}(\xi)$ and $J_{A''}(\xi)$ are displayed. Vertical dotted lines indicate boundaries of the reaction regions defined by the reaction force.

As can be seen in Figure B.6, the nature of the symmetric and antisymmetric orbital interactions are notoriously different. On the one hand, the A' totally symmetric representation is associated with π electronic reordering while A'' captures the σ activity. At first glance, it can be seen that π

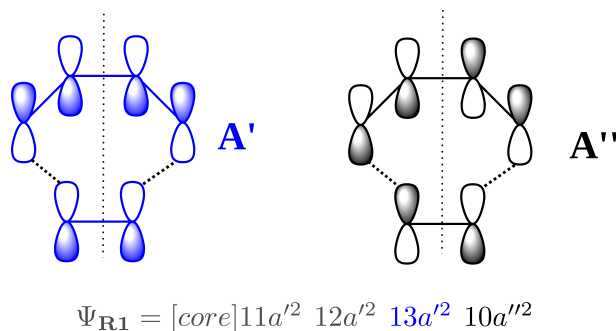


FIGURE B.5: A' and A'' orbital interactions for **R1**. The dotted line corresponds to the σ_h molecular plane. System's wave function is shown below the symmetrized orbital approaches.

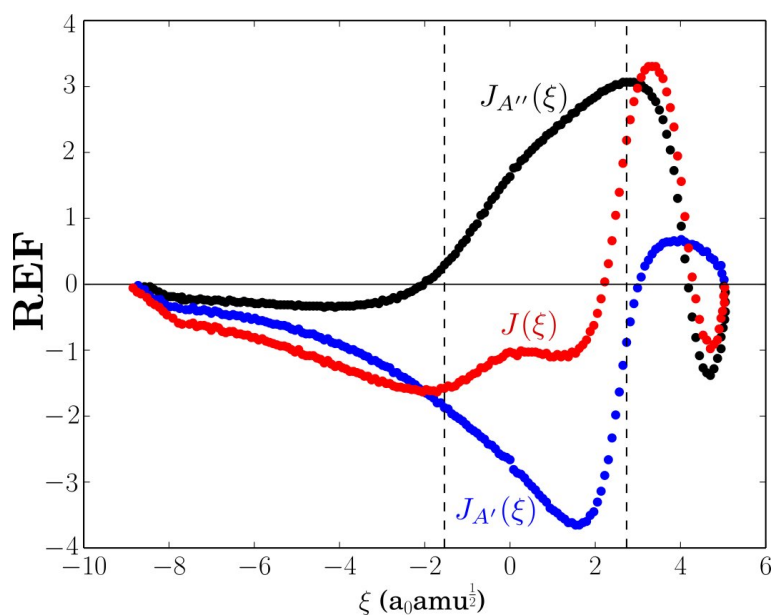


FIGURE B.6: Total, A' and A'' reaction electronic fluxes $J(\xi)$, $J_{A'}(\xi)$ and $J_{A''}(\xi)$, respectively. Flux values given in $\text{kcal}\cdot\text{mol}^{-1}\cdot(\text{a}_0\text{amu}^{1/2})^{-1}$. Vertical dotted lines corresponds to the minimum and maximum of the reaction force. They divide the reaction coordinate into reactant, transition state and product regions, respectively.

bonding changes firstly dominate the total REF. Then, within the transition state region, both σ and π electronic activity are at play although the π electronic activity prevails over the σ one. This situation is inverted short before leaving the TS region where the σ reordering takes over and leads the electronic activity until reaching the product of the reaction.

In the first stage, the interaction between diene and dienophile is inherently electrostatic (through space), which endures as an increasing polarization. This polarization promotes negative REF values indicating that bond weakening and/or making processes lead the reaction, $J(\xi)$ remains negative all along the reactant and TS regions becoming positive shortly before the product region, reaching a maximum in that region. Afterward, a final non-spontaneous electronic reorganization is evidenced until reaching the product structure.

The changes of the symmetry counterparts explain the changes in the total electronic activity, $J_{A'}(\xi)$ and $J_{A''}(\xi)$. The initial non-spontaneous electronic activity due to the approaching of the reactants is captured by $J_{A'}(\xi)$. Thus, the increasing non-spontaneity in the electronic activity is attributed to the weakening of the π bonds in both butadiene and ethylene. $J_{A'}(\xi)$ reaches a minimum after the TS structure becoming positive at the edge of the TS region. This minimum accounts for the breaking of three π bonds primitively belonging to butadiene and ethylene. Finally, the REF undergoes an abrupt change to reach positive values entering the product region. This positive peak is attributed in part to the consolidation of the new C2–C3 π -bond, which also transforms according to the A' representation.

On the other hand, the σ -flux, $J_{A''}(\xi)$, remains near a zero until it is activated entering the TS region, which means that there is only little electronic activity associated to σ bonding up to that point. This is due to the “through bond” nature of the A'' interaction, which needs sufficient orbital overlap in order to start the bond formation process, a condition that is not satisfied at the beginning of the reaction. Entering the TS region, the two fragments are sufficiently close for the bond formation process to come into effect. This is reflected by a continuously increasing $J_{A''}(\xi)$. Therefore, the positive maximum of $J_{A''}(\xi)$ corresponds to the formation of the two σ -bonds between

butadiene and ethylene, bond formation processes that together with the C2-C3 π -bond contributes to the maximum exhibited by $J(\xi)$ in the product region. The positive flux in $J_{A''}(\xi)$ is also associated to spontaneous delocalization of the electron density in order to ensure the necessary overlap for the formation of the two new σ -bonds. In the product region, a negative peak is observed which is related to low intensity electronic activity due to structural relaxation in the C1-C6 and C4-C5 bonds to reach an equilibrium structure of cyclohexene.

In summary, π electronic activity drives the reaction until reaching the product region, and triggers the σ bonding activity well advanced the reaction. From these results, it can be noticed that σ and π electronic changes do not occur at the same time along the reaction coordinate.

(R2) Formation of o-Benzynes

The pericyclic o-benzyne reaction takes place under a C_{2v} symmetry regime. As a consequence, two different types of interaction arise, which can be classified as “in-plane” and “out-of-plane” that contains σ and π electronic reordering. The total REF is therefore composed by a “in-plane” and a “out-of-plane” contribution, $J_{ip}(\xi)$ and $J_{op}(\xi)$, respectively, as follows:

$$J(\xi) = J_{ip}(\xi) + J_{op}(\xi) \quad (\text{B.7})$$

with

$$J_{ip}(\xi) = J_{A_1}(\xi) + J_{B_2}(\xi) \quad (\text{B.8})$$

$$J_{op}(\xi) = J_{A_2}(\xi) + J_{B_1}(\xi) \quad (\text{B.9})$$

On one hand, the $J_{ip}(\xi)$ is composed by the A_1 and B_2 irreducible representations, which are associated with π and σ electronic reordering, respectively. $J_{A_1}(\xi)$ ($J_{B_2}(\xi)$) flux is constructed by the $10A_1$ and $11A_1$ ($7B_2$ and $8B_2$) molecular orbitals. On the other hand, the J_{op} is composed by the A_2 and B_1 irreducible representations that are both associated to π electronic activity. $J_{A_2}(\xi)$ ($J_{B_1}(\xi)$) flux is constructed by the $1A_2$ and $2A_2$ ($2B_1$ and $3B_1$) molecular orbitals. All orbital interactions of the four irreducible representations as well as the wave function of the system are shown in Figure B.7. The $J_{ip}(\xi)$ and $J_{op}(\xi)$ fluxes together with the $J(\xi)$ are shown in Figure B.8(a). It can be observed that as the reaction advances $J_{ip}(\xi)$ responds for the most significant and percentage of the electronic activity, and therefore the *in-plane* electronic activity dominates.

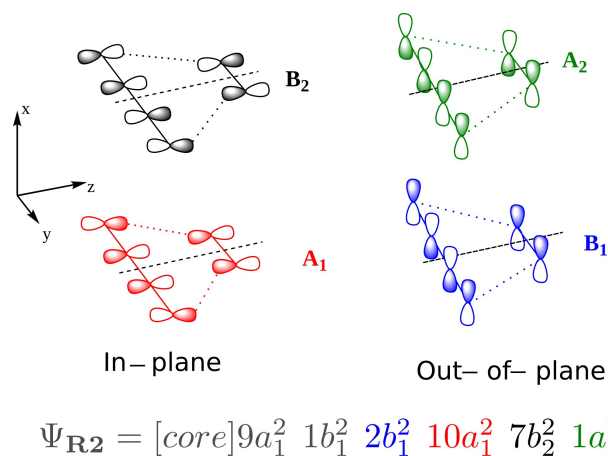


FIGURE B.7: Different orbital approaches belonging to a defined irreducible representation. The dotted lines that bisect the orbital approaches correspond to the C_2 symmetry axis and the $\sigma(xz)$ plane. The system's wave function is shown below the symmetrized orbital approaches. Each irreducible representations is represented in color code.

The $J_{ip}(\xi)$ and its components $J_{A_1}(\xi)$ and $J_{B_1}(\xi)$ are shown in Figure B.8(b). In this reaction the $J_{A_1}(\xi)$ and $J_{B_2}(\xi)$ fluxes account for π and σ bonding changes within the $\sigma'_v(yz)$ plane, respectively. From Figure B.8(b) it is shown that the antisymmetric B_2 flux governs the electronic activity. In summary, $J(\xi)$ is dominated in the reactant region by the symmetric $J_{A_1}(\xi)$ component, thus indicating that the reaction starts with π reordering. Then, entering the TS region, the electronic activity associated with the σ bonding $J_{B_2}(\xi)$, takes over and prevails until the product is formed.

A closer look into the $J_{A_1}(\xi)$ and $J_{B_2}(\xi)$ fluxes shows that $J_{A_1}(\xi)$ decreases toward negative values from the very beginning of the reaction, witnessing a non-spontaneous electronic activity. To decrease the potential energy due to orbital repulsion, the in-plane $\sigma'_v(yz)$ and π bonds start breaking processes which are captured by the $J_{A_1}(\xi)$ flux. Concomitantly a new π bond is formed between C2 and C3 (see orbital approach in Figure B.7)², which can be visualized in the $J_{A_1}(\xi)$ profile as a positive peak after the transition state structure. At the same time, the formation of the new σ bonds is visualized

²In Figure B.7, the in plane A_1 approach depicts a π type bonding between C2 and C3, which corresponds to the unique π -bond formed in-plane.

through $J_{B_2}(\xi)$ that shows practically no electronic activity in the reactant region. As in **R1**, here again, the near-zero flux regime is maintained due to the “through bond” nature of this interaction which requires an adequate orbital overlap to start the electron density transfers. Entering the TS region, spontaneous electronic changes corresponding to the formation of the new σ bonds (C1–C6 and C4–C5) are activated (see orbital approach in Figure B.7).

The out-of-plane electronic activity corresponding only to π reorganizations is found to be quite weak, it is characterized by $J_{op}(\xi)$ and composed by $J_{A_2}(\xi)$ and $J_{B_1}(\xi)$, all three shown in Figure B.8(c). When the C_4H_2 and C_2H_2 moieties are sufficiently close to each other, the parallel π orbitals overlap responding for the positive A_2 flux. At the same time, π bonds get broken accounting for the negative B_1 flux. The delocalized nature of the π system is confirmed by the fact that the above-mentioned bond-forming and breaking processes coincide, the positive and negative peaks observed in Figure B.8(c) support this observation.

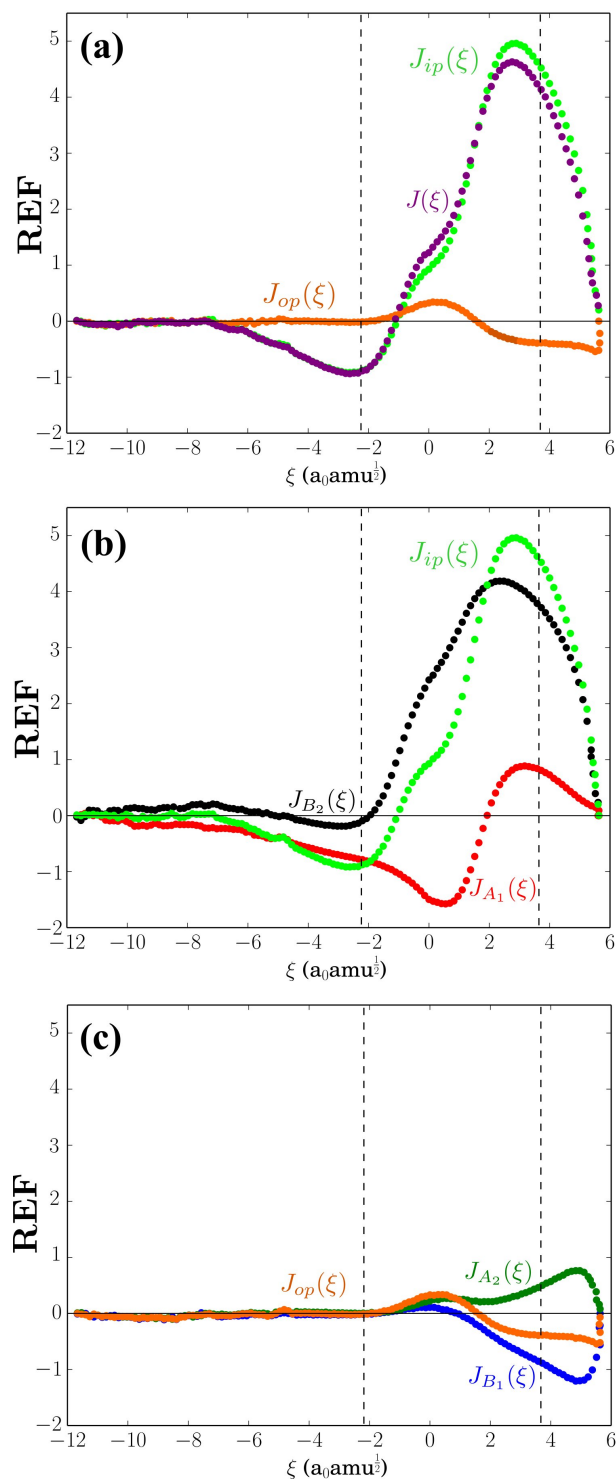


FIGURE B.8: (a) $J(\xi)$, $J_{ip}(\xi)$ and $J_{op}(\xi)$; (b) $J_{ip}(\xi)$, $J_{A1}(\xi)$ and $J_{B2}(\xi)$; (c) $J_{op}(\xi)$, $J_{A2}(\xi)$ and $J_{B1}(\xi)$ reaction electronic fluxes for reaction **R2**. Flux values given in $\text{kcal}\cdot\text{mol}^{-1}\cdot(\text{a}_0\text{amu}^{1/2})^{-1}$. Vertical dotted lines corresponds to the minimum and maximum of the reaction force.

B.3.3 Conclusions

The symmetry-adapted reaction electronic flux was computed along the reaction coordinate to characterize the electronic activity taking place along the reaction path of two representatives Diels Alder reactions. It has been found that for **R1** the the electronic activity was rationalized in terms of σ and π reorganizations. In the case of **R2**, the electronic activity was rationalized in terms of *in-plane* and *out-of-plane* fluxes.

Results indicate that the two reactions follow a similar pattern in its electronic activity; both reactions initiate with non-spontaneous electronic changes due to π reorganizations then spontaneous σ rearrangements take over. On the other hand, results described above show that the bonding changes (π and σ) do not occur concertedly.

B.4 Decomposition of the Electronic Activity in Competing [5,6] and [6,6] Cycloaddition Reactions Between C₆₀ and Cyclopentadiene

Fullerenes with potential applications in many fields that range from materials science to medicinal chemistry are important molecular entities in nanochemistry [270–272]. The most prominent representative of the fullerene family is C₆₀. This molecule behaves as a polyolefin poor in electrons (with strong electron-withdrawing character). As a result, fullerenes undergo a variety of chemical organic reactions, the most important being nucleophilic additions [273–275]. Moreover, C₆₀ reacts through many metal-catalysed processes like Pauson-Khand [276–278], Suzuki-Miyaura reactions [279–282], or [2 + 2 + 2] cycloadditions reactions [283–285]. However, one of the most frequently employed reactions for functionalization of fullerenes and their derivatives is the Diels-Alder (DA) cycloaddition [286–291]. The electron-withdrawing nature of C₆₀ makes this molecule an ideal dienophile for DA reactions [292]. The functionalization of C₆₀ through the DA reaction can yield many different products as a result of monoaddition, bisaddition and so on, up to six consecutive additions [293, 294]. In some cases, formed adducts are thermally unstable and can undergo cycloreversion [295].

C₆₀ has two different types of C-C bonds (see Figure 1). Corannulenic [5,6] bonds are located between a hexagon and a pentagon, whereas the pyracylene [6,6] bonds are found in the hexagon-hexagon ring junctions [296]. The Diels-Alder reaction in empty fullerenes show an almost exclusive preference for the [6,6] versus the [5,6] bonds [274, 275, 297, 298]. The [5,6] becomes favored or at least competitive in some endohedral metallofullerenes (EMFs) [299]. For chemists working on reactivity of fullerenes, it would be fascinating to have full control on the regioselectivity of the DA reactions. Interestingly, the [5,6] attack has been computationally predicted to be favored in strongly

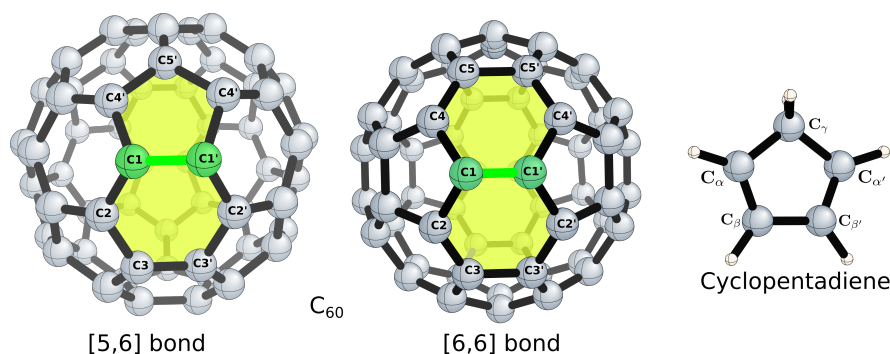


FIGURE B.9: Two types of bond in fullerene (C_{60}) schematized along with cyclopentadiene. Labeling of the relevant atoms is shown.

reduced C_{60} cages [300] and in high spin states [301]. The accumulation of negative charge or spin density takes place in the 5-membered rings (5-MRs) of C_{60} . Consequently, the aromaticity of the 5-MRs increases and the [5, 6] attack becomes preferred because it breaks the aromaticity of only an aromatic 5-MR [302], whereas the [6, 6] attack destroys the aromaticity of two aromatic 5-MRs.

In general, functionalization of fullerenes and EMFs occurs regioselectively in a unique or a few addition sites [303]. It would be desirable to have full control of the regioselectivity of additions to fullerenes and EMFs in such a way that chemists could fully determine the addition pattern in a given functionalization process. To move forward to this objective, it is necessary to have a deep understanding of the reasons for the high regioselectivity of fullerenes toward [6, 6] bonds. The main aim of the present section is to provide insight into the question of why the DA cycloaddition to C_{60} occurs exclusively at the [6, 6] bonds, using computational tools derived from the conceptual Density Functional Theory (CDFT), in particular, the symmetry-adapted reaction electronic flux.

B.4.1 Computational Details

The cycloaddition reaction between C_{60} and cyclopentadiene was studied with a well-tested DFT method. The M06-2X exchange-correlation functional was used for all atoms. The 6-31G(d) basis set was used in conjunction with Truhlar’s selected exchange correlation functional. The Berny Synchronous Transit-Guided Quasi-Newton (STQN) algorithm [304, 305] was used in searching for the TS geometries [76, 77], which were confirmed through vibrational frequency computations. Then, reactions leading toward the [5, 6] and [6, 6] reaction pathways were followed through the intrinsic reaction coordinate (ξ , IRC) by means of the IRC procedure as implemented in *Gaussian09* [78–80, 82]. All along the reaction coordinate the interaction between C_{60} (I_h) and cyclopentadiene (C_{2v}) takes place under a C_s symmetry pathway. The cutoffs used to ensure the C_s point group in the IRC computations were set to be loose (threshold of 0.1 Å). Single point calculations on the gas-phase M06-2X geometries were carried out using the domain-based local pair-natural orbital coupled cluster (DLPNO-CCSD(T)) scheme [160–164] in conjunction with the cc-pVTZ basis set [306]. Density fitting was used to compute two electron integrals [307]. The Orca 4.0.1 Software package was used for the DLPNO-CCSD(T)/cc-pVTZ computations [308].

For comparative purposes the profiles are presented in a reduced reaction coordinate (RRC, ξ_i^*) in which reactants and products at ξ_R^* and ξ_P^* are 0 and 1, respectively. Each point on the RRC (ξ_i^*) is computed as follows

$$\xi_i^* = \frac{\xi_i - \xi_R}{\xi_P - \xi_R} \quad (\text{B.10})$$

where ξ_i corresponds to point i on the IRC. For a given property A defined in both coordinates, it follows that

$$\frac{d^n A(\xi)}{d\xi^n} = \Omega_n \frac{d^n}{d\xi^{*n}} A(\xi^*), \quad \Omega_n = \frac{1}{(\xi_P - \xi_R)^n} \quad (\text{B.11})$$

B.4.2 Results and Discussion

The cycloaddition reaction between C_{60} and cyclopentadiene was computed along the reaction coordinate, energy profiles for the [5, 6] and [6, 6] pathways are displayed in Figure B.10(a). Activation energies computed at the M06-2X/6-31G(d) level were found to be 22.7 and 6.5 kcal mol⁻¹ for the [5, 6] and [6, 6] reaction pathways, while the predicted exothermicities are -4.9 and -27.1 kcal mol⁻¹ (both activation and reaction energies reported above were computed using the energies of the isolated reactants).³ As previously reported [298, 309], the occurrence of the [6, 6] cycloaddition is favored both kinetically and thermodynamically due to its relatively small activation energy and more exoenergetic character compared to that of the [5, 6] reaction. By inspection of the energy profiles shown in Figure B.10(a) it can be seen that both reaction pathways can be classified as anti-Hammond, with a late transition state closer to the product ($\xi^* > 0.5$) [310]. However, the TS in the [5, 6] is found to be much closer to the product than that on the [6, 6] path.

Experimentally, it has been found that the reaction product of the [4 + 2] cycloaddition reaction between C_{60} and cyclopentadiene only gives the [6, 6] adduct, without manifestation of subsequent ring openings [297, 311, 312]. Reactions of C_{60} with cyclopentadiene and other dienophiles have been experimentally reported, in which the cycloadducts formed are sometimes unstable and prone to revert to the formation of the initial reactants with elevation of temperature [295, 313, 314]. The available experimental data shows that the activation energy for the cycloaddition between C_{60} and cyclopentadiene is 6.9 kcal mol⁻¹ as reported by Pang and Wilson [313] which agrees very well with our findings. Furthermore, Giovane *et al.* reported an activation energy of 26.7±2.2 kcal mol⁻¹ for the corresponding retro Diels

³These values are slightly different from those coming out from the energy profiles of Figure B.10 which are not referenced to the isolated reactants.

Alder reaction [314]. From the suitable subtraction of these two numbers, the experimental reaction energy can be estimated to be -19.8 ± 2.2 kcal mol⁻¹ [309]. The activation enthalpy of reaction in terms of the reactant complex and the isolated reactants, $\Delta H^\ddagger$ and $\Delta H_{isol}^\ddagger$, for the [6,6] path in toluene solution were 18.7 and 23.9 kcal mol⁻¹, respectively. Furthermore, the corresponding reaction enthalpy energies, ΔH° and ΔH_{isol}° , were found to be -22.3 and -19.9 kcal mol⁻¹. Clearly the obtained activation energies disagree with the activation barriers experimentally obtained. The M06-2X/6-31G(d) method has been used as a part of the two-layered ONIOM approach (ONIOM2), ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G). Cyclopentadiene and the pyracenylic moiety in C₆₀ were treated with the M06-2X/6-31G(d) level of theory while the rest of carbon atoms in C₆₀ were treated with SVWN/STO-3G. With this composite method an activation energy of 8.2 kcal mol⁻¹ is obtained referenced to the reactant complex and 12.1 kcal mol⁻¹ relative to the isolated reactants, the latter very close to the experimental value [309]. For a more detailed discussion of the activation energies with respect to the level of theory, the reader is referred to ref [309].

To gain insights into the reaction mechanism, the RF was obtained, and it is displayed in Figure B.10(b). Within the RF formalism, the reaction coordinate can be divided into regions where different reaction mechanisms might be operating. The limits of the reaction regions are denoted by vertical dashed lines in black and red for the [5,6] and [6,6] reaction channels, respectively. For numerical results extracted from the RF formalism, refer to Table G.2. On one hand, it is worth noting that when the two pathways are compared, the same percentage of structural and electronic expending is exhibited: 73% of the energy barrier is mainly used in structural reorganizations to reach the TS structure, whereas only a 27% of $\Delta E^\ddagger$ accounts of electronic expenditure. This result is consistent with the work of Fernández *et al.*, where the deformation energy obtained by the activation-strain model was quite similar for the [5,6] and [6,6] attack [298]. On the other hand,

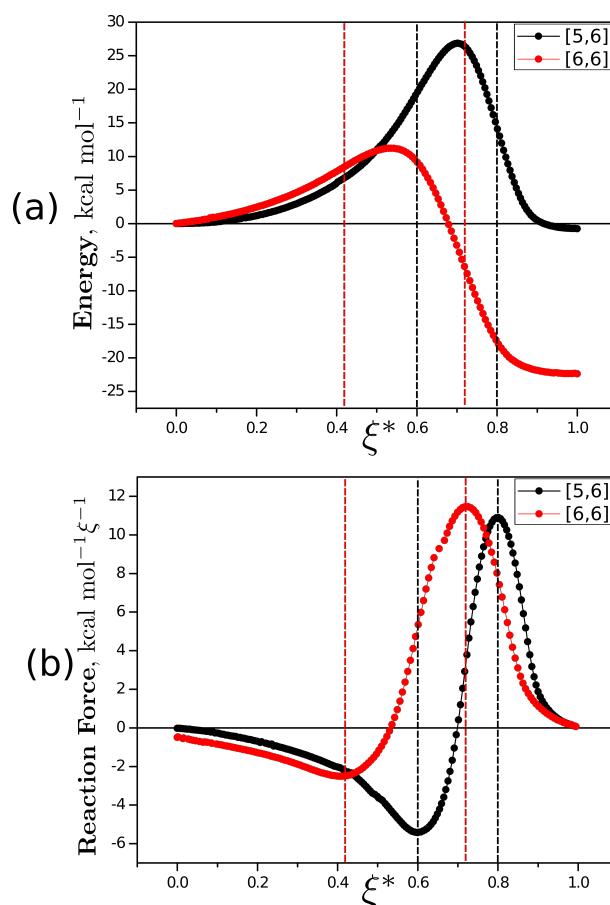


FIGURE B.10: Energy (a) and reaction force profiles (b) for the cycloaddition between C_{60} and cyclopentadiene computed in gas phase. The [5,6] and [6,6] reaction is represented in black and red, respectively. Energies computed at the M06-2X/6-31G(d) level of theory. Vertical dashed lines correspond to the minimum and maximum of the reaction force. These vertical lines divide the reaction coordinate into reactant, transition state and product regions, respectively. In the reduced reaction coordinate, $\xi^* = 0$ is the reactant complex and $\xi^* = 1$ is the product complex (both with C_s symmetry).

solely in terms of energy, clearly the [5,6] pathway exhibits both structural and electronic energies larger than the [6,6] pathway, which explains the higher activation energy obtained for the [5,6] path.

To obtain more reliability regarding the activation and reaction energies and to validate the level of theory used in this study, we have computed coupled cluster energies with single, double and perturbative triple excitations (CCSD(T)) using the DLPNO scheme as implemented in the *Orca* software. Coupled cluster energies were computed over the M06-2X geometries previously optimized, and it was verified that they correspond to a minimum or a

Reaction	$\Delta E^\ddagger$	ΔE°	$W_1(\% \Delta E^\ddagger)$	$W_2(\% \Delta E^\ddagger)$
[5, 6] pathway	26.84	-0.75	19.63 (73)	7.21 (27)
[6, 6] pathway	11.22	-22.38	8.18 (73)	3.04 (27)

TABLE B.2: Activation and reaction energies extracted from energy profiles obtained through the IRC procedure in the gas phase at the M06-2X/6-31G(d) level of theory. The reaction works (W_i) computed from the reaction force analysis are also quoted. Energetic values reported in kcal mol⁻¹.

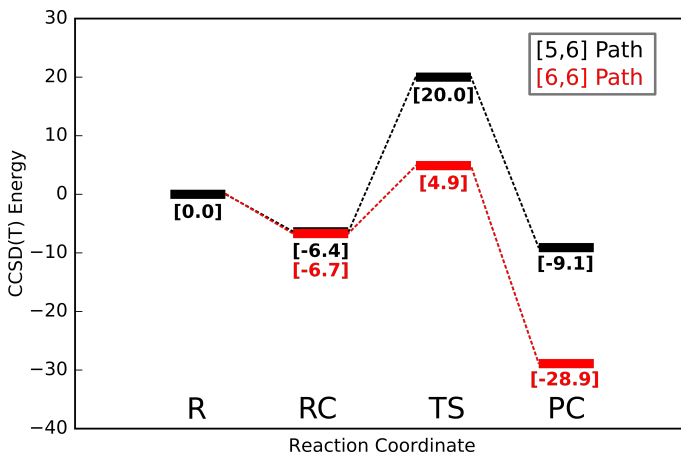


FIGURE B.11: DLPNO-CCSD(T)/cc-pVTZ energies for the [5, 6] and [6, 6] paths associated with the cycloaddition between C₆₀ and cyclopentadiene. Energetics are in kcal mol⁻¹.

transition state (see Computational Details Section). In Figure B.11, energies for both reaction pathways are presented. As may be seen from Figure B.11, the formation of the reactant complex is exoenergetic, and interestingly both reactant complexes lie roughly at the same energy. The latter result indicates that the energetic difference between both reaction paths arises after the formation of the reactant complex, and therefore the formation of it does not play a significant role in the obtention of the activation barriers. In this regard, activation energies were found to be 20.0 and 4.9 kcal mol⁻¹, while reaction energies amount to -9.1 and -28.9 kcal mol⁻¹ for the [5, 6] and [6, 6] paths. Interestingly, activation energies obtained with the M06-2X functional are very close to those predicted by DLPNO-CCSD(T). This confirms not only the reasonable choice of the methodology but also the reliability of the results here presented.

B.4.2.1 Symmetry-Adapted Reaction Electronic Flux

In this section, the SA-REF profiles are discussed. The C_s symmetry pathway in which the cycloaddition between C_{60} and cyclopentadiene takes place allows the definition of two SA-REFs: $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$, following the irreducible representation of $\mathcal{G}$. The $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$ fluxes are sensitive for π and σ bonding information, as previously reported [239]. The symmetrized orbital representation (A' and A'') along with the wavefunction of the reaction under consideration is depicted in Figure B.12. The $J_{A'}(\xi^*)$ is obtained from the symmetric $109a'$ and $110a'$ orbitals whereas $J_{A''}(\xi^*)$ is computed from the antisymmetric $89a''$ and $90a''$ orbitals. The total REF is then obtained as $J(\xi) = J_{A'}(\xi^*) + J_{A''}(\xi^*)$. It is worth noting that the $90a''$ molecular orbital for the $[5,6]$ pathway corresponds to the LUMO+1 while for the $[6,6]$ pathway the LUMO+2 is used.

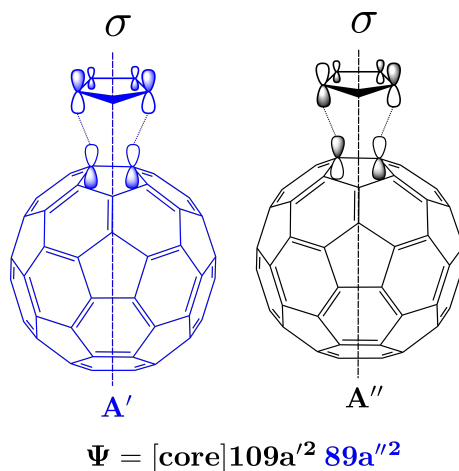


FIGURE B.12: A' and A'' orbital interactions for cycloaddition between fullerene and C_{60} . Only representative p orbitals are shown for C_{60} . The dotted lines represent the σ molecular plane. The system's electronic wave function is shown below the orbital representation.

In the present cycloaddition mechanisms (for both $[5,6]$ and $[6,6]$ paths), three π bonds are broken: one in C_{60} ($C1-C1'$) and two in cyclopentadiene ($C_\alpha-C_\beta$ and $C_{\alpha'}-C_{\beta'}$). Moreover, one π ($C_\beta-C_{\beta'}$) and two σ bonds ($C1-C_\alpha$ and $C1'-C_{\alpha'}$) are formed.

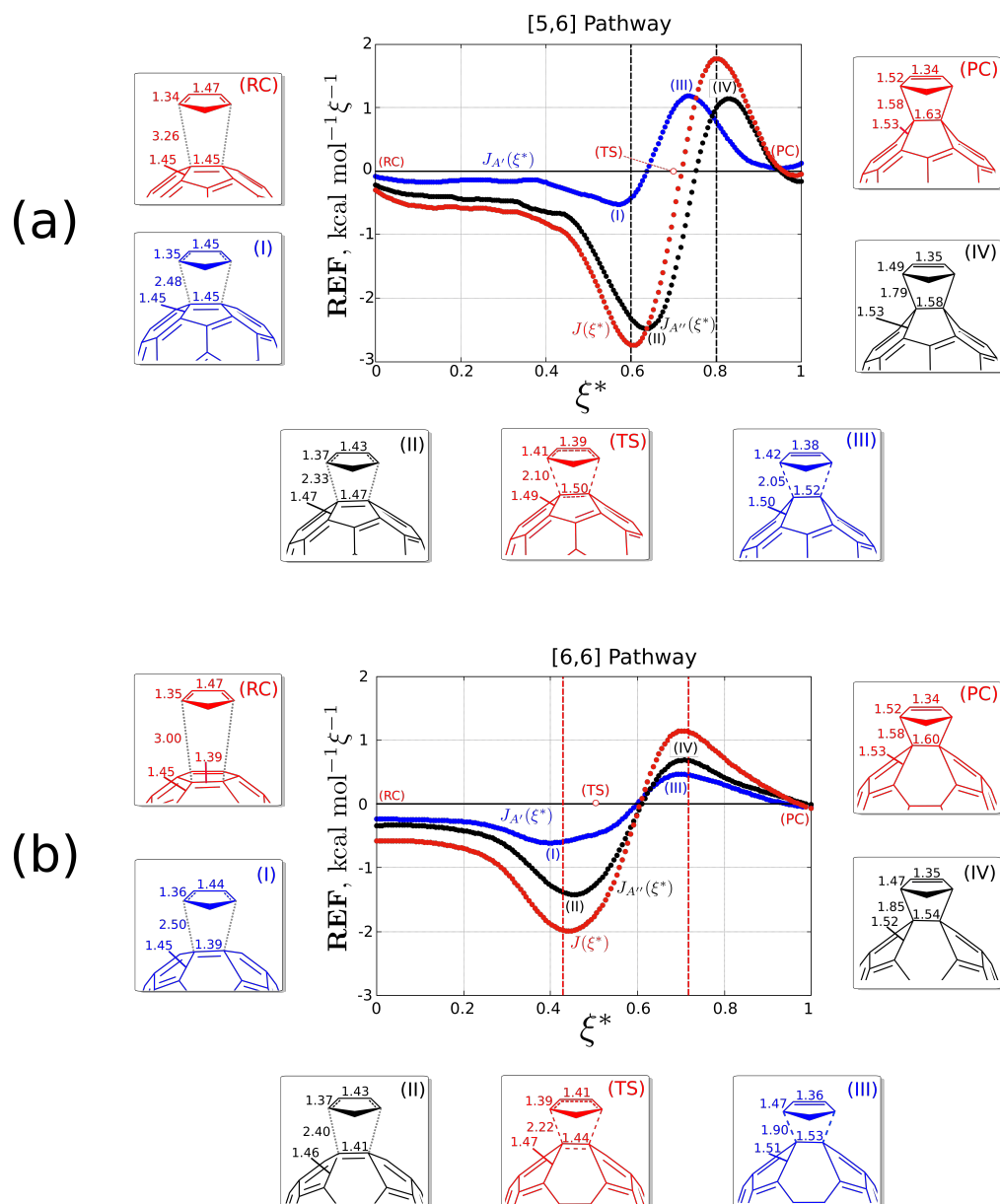


FIGURE B.13: Total, A' and A'' electron fluxes represented by $J(\xi^*)$, $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$, respectively, for the [5,6] (a) and [6,6] pathway (b). Structures at key points (labeled as **RC**, **I**, **II**, **TS**, **III**, **IV**, and **PC**) along the reaction coordinate are shown. Distances are given in Angstroms. Vertical dashed lines correspond to the minimum and maximum of the reaction force. The vertical separators divide the reaction coordinate into reactant, transition state and product regions, respectively. In the reduced reaction coordinate, $\xi^* = 0$ is the reactant complex and $\xi^* = 1$ is the product complex (both with C_s symmetry).

The total electronic activity and what accounts for π and σ reordering in the [5, 6] and [6, 6] reaction pathways are shown in Figure B.13 (a) and B.13(b), respectively. Starting with the [5, 6] path, it can be seen in the $J(\xi^*)$ profile that a non-spontaneous electronic activity starts to drive the reaction from the very beginning until reaching a minimum at the end of the **RR** (force minimum). Therefore, in the **RR**, bond weakening/breaking dominates in this region of the mechanism. At the REF minimum, the electron flux experiences a step; it increases sharply to reach a maximum at the end of the **TSR**. This change is reflected through an increment of the electronic activity, an indicator that bond-forming processes are predominant at this stage of the mechanism. Then, the total REF decreases until reaching the product complex structure with $J(\xi^*) = 0$. When the $J(\xi^*)$ are compared between the [5, 6] and [6, 6] mechanisms in Figures B.13(a) and B.13(b), respectively, it can be observed that the same electronic pattern is found for both reactions: the REF's minimum and maximum coincide with RF's minimum and maximum. However, the electron flux is more intense in the [5, 6] path than that observed in the [6, 6] path. This fact has a preponderant influence on the difference observed in the activation energies: the more intense is the electronic reordering in the activation process, the larger is the activation energy. This general pattern has been reported previously [218].

To gain more information concerning the electronic activity that takes place along the reaction, the $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$ fluxes are discussed hereafter. In general, it is observed that $J_{A''}(\xi^*)$ prevails over the $J_{A'}(\xi^*)$ for both cycloadditions along the entire reaction coordinate, although these differences are stressed at the flux minimum.

Regarding the $J_{A'}(\xi^*)$ profile for the [5, 6] path (Figure B.13(a)), it is negative all along the **RR**. The main event here is the weakening of the π bonds centered in the C1-C1' bond in fullerene and the C_α - C_β and $C_{\alpha'}$ - $C_{\beta'}$ bonds in cyclopentadiene (see Figure B.9 for labeling of atoms). A strong Pauli

electrostatic repulsion prompts the weakening and subsequent breaking of these bonds as the reactants approach one another [202, 239]. At the $J_{A'}(\xi^*)$ minimum denoted by **(I)**, it is observed that the C_α - C_β and $C_{\alpha'}$ - $C_{\beta'}$ bonds have changed by only 0.01 Å. The C1-C1' bond remains unchanged for the **(RC)** structure, which supports the idea that up to this point weakening over breaking processes is found. Subsequent to **(I)** the π electronic activity, captured by $J_{A'}(\xi^*)$, is driven toward positive values passing through the **(TS)** structure and reaching a maximum at **(III)**. It is worth noting that at the TS structure the C_α - C_β and C_β - $C_{\beta'}$ bond distances are very close with values of 1.41 and 1.39 Å, respectively, denoting a highly delocalized cyclopentadiene moiety. At **(III)**, the formation of the πC_β - $C_{\beta'}$ bond is completed, according to the $J_{A'}(\xi^*)$ pattern. Afterward, the π electronic activity decreases toward zero, where the π bonds both in fullerene and cyclopentadiene are formed.

The $J_{A''}(\xi^*)$ profile for the [5,6] path shows the electronic reordering for σ electrons according with the SA-REF scheme (Figure B.13(a)). In the $J_{A''}(\xi^*)$ profile the electronic activity also decreases from the onset of the reaction until reaching a minimum at **(II)** located within the **TSR**. This non-spontaneous electronic activity is observed due to the weakening of the σ bonds neighboring the C1 and C1' carbon atoms in fullerene, as a consequence of the pyramidalization of the atoms mentioned above in the transition $sp^2 \rightarrow sp^3$. This negative peak has not been observed before for similar DA reactions [239]. When the electronic activity reaches a minimum, it increases sharply until it encounters a maximum at **(IV)**. At this spontaneous reordering, the formation of the cycloadduct through the synchronous formation of the two σ bonds between C1- C_α and C1'- $C_{\alpha'}$ is evidenced. At the **(IV)** stage, the bond distance of the C1- C_α and C1'- $C_{\alpha'}$ is 1.79 Å, suggesting a loosely bonded complex. Afterward, the electronic activity decreases toward the equilibrium condition, reaching zero. At the **(PC)** structure the σ bonds formed at **(IV)** are strengthened and they acquire a distance of

1.58 Å. Moreover, it is worth mention that an adjacent bond to the C1-C1' has been tracked along the reaction coordinate from **(RC)** to **(PC)**, and has been selected to account for the pyramidalization toward the formation of the new simple bonds. As may be seen, this bond changes in length from 1.45 to 1.53 Å. Similar distortions take place in the vicinal bonds to start the σ bond formation.

Regarding the [6, 6] fluxes, similar tendencies and results are extracted from $J(\xi^*)$, $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$ (Figure B.13(b)). The minimum and maximum of the REF and SA-REFs have the same interpretation as those observed for the [5, 6] reaction pathway. Furthermore, some differences along the two reaction paths will be discussed hereafter. Since some differences in terms of the total REF were discussed above, special attention will be devoted to the SA-REFs, to find differences along the two competitive paths. When the $J_{A'}(\xi^*)$ is compared between both pathways (Figures B.13(a) and B.13(b)) it can be seen that both minima lie at the same magnitude ca. $-0.5 \text{ kcal mol}^{-1}\xi^{-1}$, whereas the maximum in these profiles differs slightly, being of larger magnitude for the [5, 6] pathway than for the [6, 6] one. As shown in ref. [298], this difference can be attributed to the weaker orbital interactions along the reaction coordinate for the [5, 6] attack as compared to the [6, 6] path. It is inferred that a larger π reorganization is needed for the [5, 6] path, due to a stronger Pauli electrostatic repulsion takes place on this path [298].

A larger difference in both reaction mechanisms that have a direct consequence in the observed activation barriers is the minimum observed by entering the **TSR** in the $J_{A''}(\xi^*)$ profile. As can be observed from the $J_{A''}(\xi^*)$ profiles in Figures B.13(a) and B.13(b), the $J_{A''}(\xi^*)$ reaches a minimum with magnitude $|J_{A''}(\xi^*)| = 2.5$ and $|J_{A''}(\xi^*)| = 1.5 \text{ kcal mol}^{-1}\xi^{-1}$ for the [5, 6] and [6, 6] paths, respectively. This difference is associated with the fact that larger energy is needed to distort the corannulenic moiety concerning the

pyracenylic fragment in the [6, 6] path, in the transition $sp^2 \longrightarrow sp^3$ of the C1 and C1' carbon atoms. This argument is reinforced since the TS in the [5, 6] path is more product-like than that in the [6, 6] path, and therefore in this former path more energy is required to distort the reactants up to the transition state structure. This energy required for a larger reorganization of the σ electrons contributes to a higher energy barrier.

B.4.2.2 Symmetry-Adapted Kinetic Energy

The kinetic energy of the electrons comes from the application of a one-electron Hermitian operator whose eigenvalues do not vary through a symmetry operation. On this basis, the obtention of kinetic energy values belonging to different irreducible representations is possible given the molecular symmetry.

In Figure B.14, the kinetic energies associated with each irreducible representation of the C_S point group are shown for each reaction path. $T_{A'}(\xi^*)$ and $T_{A''}(\xi^*)$ represent the kinetic energies of the electrons that occupy the orbitals that transform as the A' and A'' irreducible representations, respectively. In Figure B.14(a), the $T_{A'}(\xi^*)$ for both reactions are shown. In this plot two maxima are seen that account for the π electronic activity, and they are located at $\xi^* \approx 0.5$ and $\xi^* \approx 0.3$ (for the [5, 6] and [6, 6] reaction, respectively), which are almost at the same position of the respective $J_{A'}(\xi^*)$ values shown in Figures B.13(a) and B.13(b). At the same time, a minimum for both pathways is observed (once leaving the respective **TSR**) that lies almost at the same position where the maximum of the $J_{A'}(\xi^*)$ is observed in Figures B.13(a) and B.13(b). This decrease of the kinetic energy for both irreducible representations in the vicinity of the transition state structure can be attributed to the increase in aromaticity of the transient species [315–317] with delocalized electrons that have lower kinetic energy [318].

The variation of the kinetic energy along the path indicates that when a bond is being weakened or broken (negative REF values) an increase in the kinetic energy is observed, which promotes a contraction of the electronic density. Conversely, when a bond is being formed or strengthened, a decrease of the kinetic energy is observed, promoting an expansion of the electronic density. Such a pattern has been reported previously by Doubleday and Houk for a series of Diels-Alder reactions [319]. The authors obtained the mean kinetic energy from molecular dynamics and plotted it against the forming C–C bond distances. It was found that in the transition zone, a dip in the mean kinetic energy is observed. As the C–C bond stretching dominates the transition vector for Diels-Alder reactions, the kinetic energy is a good proxy for the “flux”⁴ along the reaction coordinate. This is in agreement with our results in which the minima/maxima observed in the REF profiles are in close agreement with the maxima/minima observed in the kinetic energy plots. The same conclusion can be drawn by inspection of the $T_{A''}(\xi^*)$ values with respect to the $J_{A''}(\xi^*)$ minima and maxima.

It is worth mention that in Figure B.14(a) both kinetic energy profiles follow quite similar trends, although they appear shifted one with respect to the other along ξ^* . However, in Figure B.14(b) a huge difference in the $T_{A''}(\xi^*)$ energy is found at the maximum for both reaction pathways. The maximum mentioned above lies almost at the same position where weakening of the σ bonds is carried out, which is observed as a negative peak in the $J_{A''}(\xi^*)$ profiles in Figures B.13(a) and B.13(b). Interestingly, the difference in magnitude of the negative peak observed in the $J_{A''}(\xi^*)$ profile for both reaction pathways can be understood by the positive peaks observed in $T_{A''}(\xi^*)$. Thus, the larger σ electronic activity observed in the [5, 6] path caused by the weakening of the σ bonds neighboring the C1 and C1' carbon

⁴The “flux” reported by Doubleday and Houk differs from the definition of the REF, which comes from the change of the electronic chemical potential. The “flux” is referred to the fingerprint of transition state theory, i.e., the TS is the minimum flux of forward-moving trajectories – the dynamical bottleneck.

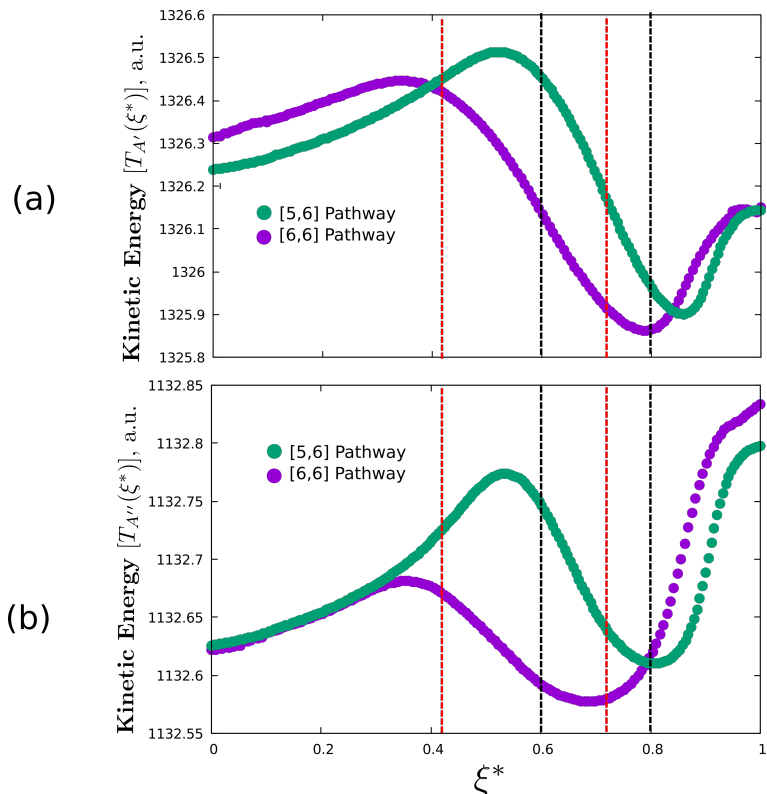


FIGURE B.14: Kinetic energies computed for each irreducible representation ($T_{\Gamma_i}(\xi^*)$) along the reaction coordinate. Reported are (a) A' kinetic energy $[T_{A'}(\xi^*)]$ and (b) A'' kinetic energy $[T_{A''}(\xi^*)]$ for the [5,6] and [6,6] reaction pathways. Vertical dashed lines correspond to the minimum and maximum of the reaction force; they are black and red for the [5,6] and [6,6] paths, respectively. These vertical lines divide the reaction coordinates into reactant, transition state and product regions, respectively. In the reduced reaction coordinate, $\xi^* = 0$ is the reactant complex and $\xi^* = 1$ is the product complex (both with C_s symmetry).

atoms (prompted by the $sp^2 \rightarrow sp^3$ transition) is entirely consistent with larger kinetic energy for those σ electrons.

B.4.3 Conclusions

We have analyzed the two reaction mechanisms of the cycloaddition reaction between C_{60} and cyclopentadiene corresponding to the [5,6] and [6,6] attacks. Partition of the total reaction electronic flux $J(\xi^*)$ into $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$ contributions allowed us to understand whether π and/or σ bonding changes take place along the progress of the reaction. The $J_{A'}(\xi^*)$ facilitates understanding the π reordering, whereas $J_{A''}(\xi^*)$ accounts for σ bonding

changes. It was found that the [6, 6] path prevails over the [5, 6] due to lower activation energy and greater exothermicity. With the use of the SA-REF it was found that the dominating event that drives the appearance of the differences in activation energies between the [5, 6] and [6, 6] path is due to a non-spontaneous σ electronic activity, which appears as a result of the weakening of the C–C bonds due to pyramidalization of the C1, C1', C $_{\alpha}$ and C $_{\alpha'}$ carbon atoms. Inspection of the kinetic energy of both irreducible representations showed that when a bond is being weakened/broken (negative values of REF) an increase in the kinetic energy occurs which we associate with a contraction of the electronic density in the vicinity of the chemical event. Conversely, when a bond is being formed/strengthened (positive REF values) a decreasing of the kinetic energy is observed, and therefore, an expansion of the electronic density occurs. Moreover, the decrease of the kinetic energy of electrons supposes the increase in aromaticity in the vicinity of the transition state. The SA-REF is a useful tool derived from a global property that gives valuable information about local bonding changes taking place along a reaction pathway. From the detailed characterization and rationalization of the chemical events in the present contribution, modulation of reactivity could be achieved as desired, thus controlling the regioselectivity of this kind of reactions.

B.5 Concluding Remarks

In this chapter, the mechanism of three Diels-Alder reactions has been analyzed employing the symmetry-adapted reaction electronic flux. The SA-REF takes advantage of the irreducible representations of a point group which is conserved along the entire reaction coordinate. Moreover, the SA-REF can be seen as a useful tool when direct Koopmans' and finite difference approximations fail to compute the chemical potential. From the characterization of the electronic activity it has been shown that the SA-REF can also give valuable information regarding $\sigma - \pi$, *in-plane*, and *out-of-plane* electronic reorderings. In this chapter, the SA-REF was also studied together with the kinetic energy according to its irreducible representation counterparts. From the results, it was concluded that when a bond is being weakened or broken (negative REF values) an increase in the kinetic energy is observed, which promotes increment in the chemical potential, a contraction of the electronic density that is observed as a lowering in the total reaction electronic flux. On the contrary, when a bond is being formed or strengthened, a decrease of the kinetic energy is observed, which promotes a decreasing in the electronic chemical potential promoting an expansion of the electronic density that is observed as an increment in the $J(\xi)$. All these observations have been summarized below.

Bond Breaking: $\uparrow T \Rightarrow \uparrow \mu \Rightarrow \downarrow \rho(\mathbf{r}) \Rightarrow \downarrow J(\xi)$

Bond Formation: $\downarrow T \Rightarrow \downarrow \mu \Rightarrow \uparrow \rho(\mathbf{r}) \Rightarrow \uparrow J(\xi)$

Appendix C

Gibbs Free Energies: The quasi-RRHO method

When the harmonic approximation is used for computing thermodynamic properties, errors and numerical noise due to low-lying vibrational frequencies may arise. Therefore, in order to correct the vibrational entropy and the resulting Gibbs free energy, the quasi-rigid rotor harmonic oscillator (quasi-RRHO) method is used. This method enables to correct the vibrational entropy (S_v) by interpolation with an effective rotational entropy S_r . The vibrational entropy is computed as:

$$S_v = R \sum_{k=1}^{3M-6} \left(\frac{\Theta_{\omega_k}/T}{e^{\Theta_{\omega_k}/T} - 1} - \ln(1 - e^{-\Theta_{\omega_k}/T}) \right) \quad (\text{C.1})$$

where $\Theta_{\omega_k} = h\omega_k/k_B$ is the vibrational temperature, h is the Planck's constant, ω_k is the k -th vibrational mode, k_B is the Boltzmann's constant, T is the absolute temperature, R is the usual gas constant, and M corresponds to the number of atoms. Since the term $\frac{\Theta_{\omega_k}/T}{e^{\Theta_{\omega_k}/T} - 1}$ approaches infinity when $\omega \rightarrow 0$, the vibrational entropy is corrected by replacing it by a corresponding rotational entropy (quasi-RRHO approach) for low frequency modes.

For any real normal mode the moment of inertia μ for a free-rotor is computed as follows:

$$\mu_k = \frac{h}{8\pi^2\omega_k} \quad (\text{C.2})$$

To define an effective moment of inertia (μ') and to restrict it to a reasonable value, an average molecular moment of inertia, B_{av} , is introduced as a limiting value for very small ω (large μ).

$$\mu' = \frac{\mu B_{av}}{\mu + B_{av}} \quad (\text{C.3})$$

Usually B_{av} is set to be 1×10^{-44} kg m². However, B_{av} can also be computed as the average of the eigenvalues of the moment of inertia tensor ($\mathbf{I}$) by using normal coordinates with the center of mass as the origin of the coordinate system for each vibrational mode. The $\mathbf{I}$ tensor is:

$$\mathbf{I} = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \quad (\text{C.4})$$

with diagonal elements:

$$I_{xx} = \sum_i^M m_i(y_i^2 + z_i^2) \quad (\text{C.5})$$

$$I_{yy} = \sum_i^M m_i(x_i^2 + z_i^2) \quad (\text{C.6})$$

$$I_{zz} = \sum_i^M m_i(x_i^2 + y_i^2) \quad (\text{C.7})$$

and off-diagonal elements:

$$I_{xy} = I_{yx} = - \sum_i^M m_i x_i y_i \quad (\text{C.8})$$

$$I_{xz} = I_{zx} = - \sum_i^M m_i x_i z_i \quad (\text{C.9})$$

$$I_{yz} = I_{zy} = - \sum_i^M m_i y_i z_i \quad (\text{C.10})$$

Once μ' is computed, the entropy for a low-frequency mode in this approximation is computed by,

$$S_r = R \left[1/2 + \ln \left\{ \left(\frac{8\pi^3 \mu' k_B T}{h^2} \right)^{1/2} \right\} \right] \quad (\text{C.11})$$

In order to interpolate between harmonic vibrational and rotational approximations, S_v and S_r are combined by using a weighting function depending on ω_k as

$$S = w(\omega_k) S_v + [1 - w(\omega_k)] S_r \quad (\text{C.12})$$

in which $w(\omega_k)$ is given by the Head-Gordon damping function with $\alpha = 4$:

$$w(\omega_k) = \frac{1}{1 + (\omega_0/\omega_k)^\alpha} \quad (\text{C.13})$$

This function interpolates between the harmonic vibrational entropy (for $\omega \gg \omega_0$) and a pure (and always finite) rotational entropy for small ω . A value of $\omega_0 = 100 \text{ cm}^{-1}$ is recommended by Grimme as default (about $0.5k_B T$ at 298.15 K) [85]. Therefore, Equation C.12 effectively replaces the vibrational entropy for all modes with frequencies lower than $\omega_0 \text{ cm}^{-1}$ by a corresponding free-rotor entropy. In Figure C.1, S_v , S_r and interpolated entropy S are plotted using $\omega_0 = 100 \text{ cm}^{-1}$.

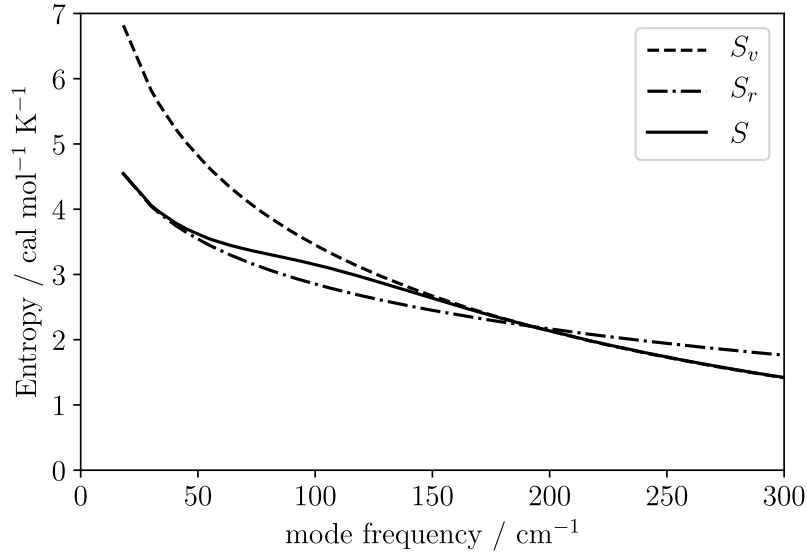


FIGURE C.1: Vibrational, rotational and interpolated entropy as a function of ω_k at $T = 298.15$ K with $\omega_0 = 100$ cm^{-1} . The B_{av} term was computed using the eigenvalues of the moment of inertia tensor for each vibrational mode.

As noted above, the cutoff ω_0 is a tuning parameter. In Figure C.2 a systematic variation of the ω_0 parameter and its effect on the interpolated entropy is shown. As can be seen, the value of the interpolated entropy is quite constant in the range 169.3–171.9 $\text{cal mol}^{-1} \text{K}^{-1}$ for the variation $\omega_0 = [100, 250]$ cm^{-1} . However, for ω_0 lower than 100 cm^{-1} , an increase in the total entropy is observed (as expected) due to the S_v has a higher preponderance.

Once the interpolated entropy is computed, the thermal free energy correction (G_{corr}) is computed as follows:

$$G_{corr} = H_{corr} - TS_{tot} \quad (\text{C.14})$$

where

$$H_{corr} = E_{tot} + k_B T \quad (\text{C.15})$$

$$E_{tot} = E_t + E_r + E_v + E_e \quad (\text{C.16})$$

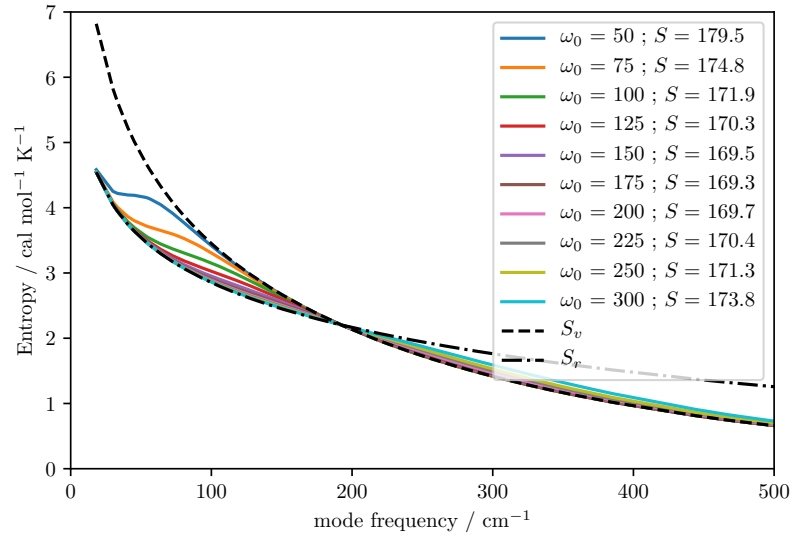


FIGURE C.2: Computed entropy as a function of ω_k at $T = 298.15$ K with variable ω_0 in the range $[50, 300]$ cm $^{-1}$. B_{av} computed by using the eigenvalues of the moment of inertia tensor for each vibrational mode.

$$S_{tot} = S + S_t + S_r + S_e \quad (\text{C.17})$$

Subindices t , r , v and e stand for translational, rotational, vibrational and electronic contributions. The reader is referred to references [320, 321] for a detailed discussion of partition functions and thermodynamical quantities.

Appendix D

Relativistic Effects

D.1 Theory

To develop some review on the DKH relativistic approximation, the Dirac's one-electron Hamiltonian has to be employed, which has the following form:

$$h_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)c^2 + V_{nuc} \quad (\text{D.1})$$

where $\boldsymbol{\alpha}$ is a three-vector containing Pauli's spin matrices on the off-diagonal, β is a diagonal matrix with entries (1,1,-1,-1), c is the speed of light, and V_{nuc} the external potential. The stationary Dirac equation in atomic units is therefore

$$h_D\Psi = (c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)c^2 + V_{nuc})\Psi = E\Psi \quad (\text{D.2})$$

The spinor Ψ can be decomposed in its so-called large and small components

$$\Psi = \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix} \quad (\text{D.3})$$

These components are coupled through the Dirac equation. Thus, upon solving for Ψ_S , the following relation is obtained:

$$\Psi_S = \frac{1}{2c} \left(1 + \frac{E - V}{2c^2} \right)^{-1} \boldsymbol{\sigma} \cdot \mathbf{p} \Psi_L = R \Psi_L \quad (\text{D.4})$$

By using an unitary transformation U ,

$$U = \begin{pmatrix} \Omega_+ & -R^+ \Omega \\ R \Omega_+ & \Omega_- \end{pmatrix} \quad (\text{D.5})$$

with $\Omega_+ = \frac{1}{\sqrt{1+R^+R}}$ and $\Omega_- = \frac{1}{\sqrt{1+RR^+}}$, the Hamiltonian can be obtained with a block-diagonal form

$$U^\dagger h_D U = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix} \quad (\text{D.6})$$

As it can be seen from the above equation, the block-diagonalized Dirac Hamiltonian is decomposed into two parts: one part solely describes electrons (h_+), while the other gives rise to negative-energy states (h_-), which are the so-called positronic states. Thus, the (electronic) large component has to satisfy the following relation

$$h_+ \Psi_L = \Omega_+ (h_+ + h_\pm R + R^+ (h_\mp + h_- R)) \Omega_+ \Psi_L = E_+ \Psi_L \quad (\text{D.7})$$

Different methods such as the zeroth-order regular approximation (ZORA) and the DKH approximation substitute the exact relation in Eq. (D.7) with approximated ones.

D.1.1 Douglas-Kroll-Hess Approximation

The DKH method expands the exact relation in Eq. (D.7) in the external potential V_{nuc} . The first-order DKH Hamiltonian is given by

$$h_+^{(1)} = E_p + A_p V_{nuc} A_p + B_p V^{(p)} B_p \quad (\text{D.8})$$

with

$$E_p = \sqrt{c^4 + c^2 p^2}, \quad A_p = \sqrt{\frac{E_p + c^2}{2E_p}}, \quad B_p = \frac{c}{\sqrt{2E_p(E_p + c^2)}} \quad (\text{D.9})$$

On the other hand, the second-order Hamiltonian has the following form

$$h_+^{(2)} = h_+^{(1)} + \frac{1}{2}[W_p, O] \quad (\text{D.10})$$

where

$$\{W_p, E_p\} = \beta O, \quad O = A_p[R_p, V]A_p, \quad R_p = \frac{c\sigma p}{E_p + c^2} \quad (\text{D.11})$$

The DKH Hamiltonian contains all spin-free, relativistic correction terms, e.g., the mass-velocity and Darwin terms which are not entirely included in the ZORA approximation. Furthermore, as the potential is included linearly, no scaling or model potential is necessary to introduce the correct behavior of the energy when an infinitesimal change in the potential is done. This characteristic makes DKH Hamiltonians be commonly used for relativistic studies.

D.2 Results and Discussion

D.2.1 Energetic Comparison

In this section, numerical tests are displayed with the aim of finding possible differences in electronic activation and reaction energies for the CO₂ activation mechanism. M06-2X/LANL2DZ/6-31G(d,p) single point computations using the DKH Hamiltonian were performed over the gas-phase structures, labeled as DKH1. Moreover, single point computations were performed with the DKH Hamiltonian employing the larger def2-TZVP basis set over the

optimized gas phase structures obtained with the M06-2X/LANL2DZ/6-31G(d,p) level of theory, labeled as DKH2. Results for activation and reaction energies are summarized in Table D.1. For the sake of comparison, only electronic energies are reported.

Reaction	LT ^a		DKH1 ^b		DKH2 ^c	
	$\Delta E_e^\ddagger$	ΔE_e°	$\Delta E_e^\ddagger$	ΔE_e°	$\Delta E_e^\ddagger$	ΔE_e°
(1 + CO2)@R1	22.75	-22.72	22.79	-22.65	19.53	-25.41
(1 + CO2)@R2	22.59	-21.33	22.65	-21.25	19.55	-24.96
(2 + CO2)@R1	16.26	-22.44	16.32	-22.41	16.95	-20.83
(2 + CO2)@R2	18.64	-20.52	18.63	-20.47	17.32	-20.11
(3 + CO2)@R1	13.34	-22.84	13.39	-22.75	13.91	-20.16
(3 + CO2)@R2	15.11	-21.45	15.14	-21.48	14.94	-19.67
(4 + CO2)@R1	9.43	-22.43	9.44	-22.46	9.78	-18.42
(4 + CO2)@R2	9.37	-22.04	9.49	-21.94	9.95	-18.77

^aLT: M06-2X/LANL2DZ/6-31G(d,p) energies

^bDKH1: DKH-M06-2X/LANL2DZ/6-31G(d,p) energies

^cDKH1: DKH-M06-2X/def2-tzvp energies

TABLE D.1: Electronic energies with/without relativistic DKH Hamiltonian

From Table D.1 it can be observed that computations with the LT and DKH1 level of theory predict a quite similar activation and reaction energies. Changes in activation and reaction energies do not follow any different trend from the M06-2X results when going down in the group, as would be expected. On the other hand, computations with the DKH2 exhibit more significant changes in the prediction of activation and reaction energies. Furthermore, the DKH2 with the inclusion of a more extensive basis set yields higher deviations for LT, but still below 3.22 kcal mol⁻¹ (Si) and ~ 1.3 kcal (Ge, Sn, and Pb). From the results, it is concluded that the inclusion of explicit relativistic effects on the study of reaction energetics does not change these quantities significantly. The latter could be easily attributed to cancellation errors. In the next section we shall see that although relativistic effects leave almost unaffected activation and reaction energies, they are necessary to account for the right interpretation of reactivity when molecular orbitals are used.

D.2.2 Relativistic Effects on Frontier Molecular Orbitals

In this section, a comparative analysis in term of the frontier molecular orbital densities is done by using the LT and DKH2 level of theory. The latter comparison is made since a more significant variation when comparing LT and DKH2 energetics was observed. Figure D.1 contains HOMO, LUMO and dual descriptor isosurfaces for system 4. As can be seen in Figure D.1(a) the HOMO density is located both at the hydride atom as well as the nitrogen atoms and *p*-carbon atom located in the NacNac backbone ring of complex 4. It is worth to mention that no density is observed over the lead atom, which would be responsible for the lone pair of electrons. When the LUMO surface is analyzed, lobes appears just in the N-C-C-C-N moiety of the NacNac ligand. Regarding the HOMO density, it should exhibit the existence of the lone pair of electrons located on the Pb atom; it is a clear signal that the relativistic effect would play an essential role in this system. Frontier orbital densities were computed at the DKH2 level of theory and displayed in Figure D.1(b). Interestingly, the HOMO and LUMO densities exhibit contribution from the Pb atom. It is because the Pb atom contains a lone pair and a vacant *p* orbital which explains the lobes. On the other hand, the contribution of the hydride atom to the HOMO density disappears altogether, which is not consistent due to the nucleophilic nature of it. Furthermore, the contribution from the NacNac ligand remains almost unchanged. From the dual descriptor results, the same results are extracted. The most noticeable difference between both levels of theory is that for the DKH2 level of theory, the Pb atom is found to be ambiphilic.

As a summary, the inclusion of scalar relativistic effects on the molecular Hamiltonian have a more substantial effect on reactivity rather than in energy differences. Similar activation and reaction energies when comparing

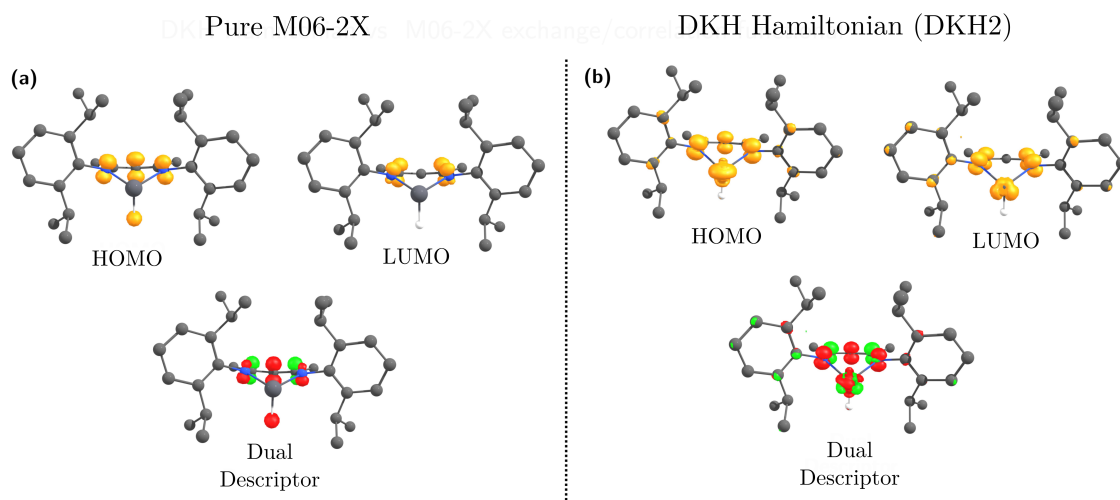


FIGURE D.1: HOMO, LUMO and dual descriptor obtained by using the M06-2X/6-31G(d)/LANL2DZ (a) and the DKH hamiltonian (DKH2 level of theory) (b).

relativistic and non-relativistic energies were found, which is due to cancellation errors. However, in terms of reactivity, larger effects have been found, in which the change of the reactivity nature of the Pb atom and hydride are profoundly affected.

Appendix E

Benchmark $\text{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\text{INT}_{2-\text{Oo}}$

functional	rung	$\text{INT}_{2-\text{Oo}}^{\text{LA}}$	$\text{INT}_{2-\text{Oo}}$
B3LYP	hGGA	RC	PC
B3LYP-D3BJ	hGGA	✓	✓
B3P86	hGGA	RC	PC
O3LYP	hGGA	RC	PC
APF	hGGA		PC
APFD	hGGA	✓	✓
ω B97-XD	hGGA	RC	✓
PBE0	hGGA	RC	RC

TABLE E.1: Benchmark computations on $\text{INT}_{2-\text{Oo}}^{\text{LA}}$ and $\text{INT}_{2-\text{Oo}}$ structures. Structures were optimized from the respective M06-2X structure and verified by frequency calculations. The 6-31G(d,p) was used for second-row atoms while LANL2DZ was used for Ge.

functional	rung	$\mathbf{INT}_{2-Oo}^{LA}$	$\mathbf{INT}_{2-Oo}$
M05	hGGA	RC	PC
M05-2X	hGGA	✓	✓
M06	hGGA	RC	PC
M06-2X	hGGA	✓	✓
M06-HF	hGGA	✓	✓
M08-HX	hGGA	✓	✓
M11	hGGA	RC	✓
SOGGA11X	GGA	RC	PC
N12SX	hGGA	✓	✓
MN12SX	hGGA	✓	✓
MN15	hGGA	✓	✓
CAM-B3LYP	LRC	RC	RC

TABLE E.2: Benchmark computations on $\mathbf{INT}_{2-Oo}^{LA}$ and $\mathbf{INT}_{2-Oo}$ structures. Structures were optimized from the respective M06-2X structure and verified by frequency calculations. The 6-31G(d,p) was used for second-row atoms while LANL2DZ was used for Ge.

Appendix F

Symmetry-Adapted Reaction Electronic Flux in Cycloaddition Reactions

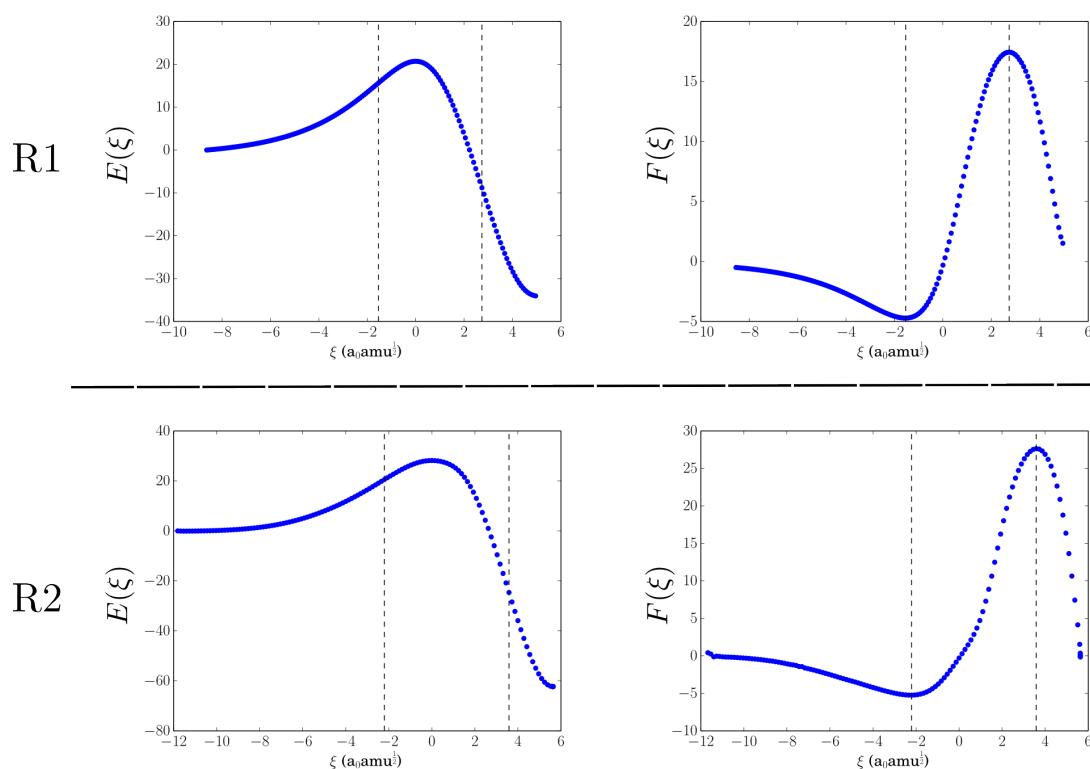


FIGURE F.1: Energy and reaction force profile for each reaction. Energy and reaction force values are given in kcal mol⁻¹ and kcal mol⁻¹ξ⁻¹, respectively.

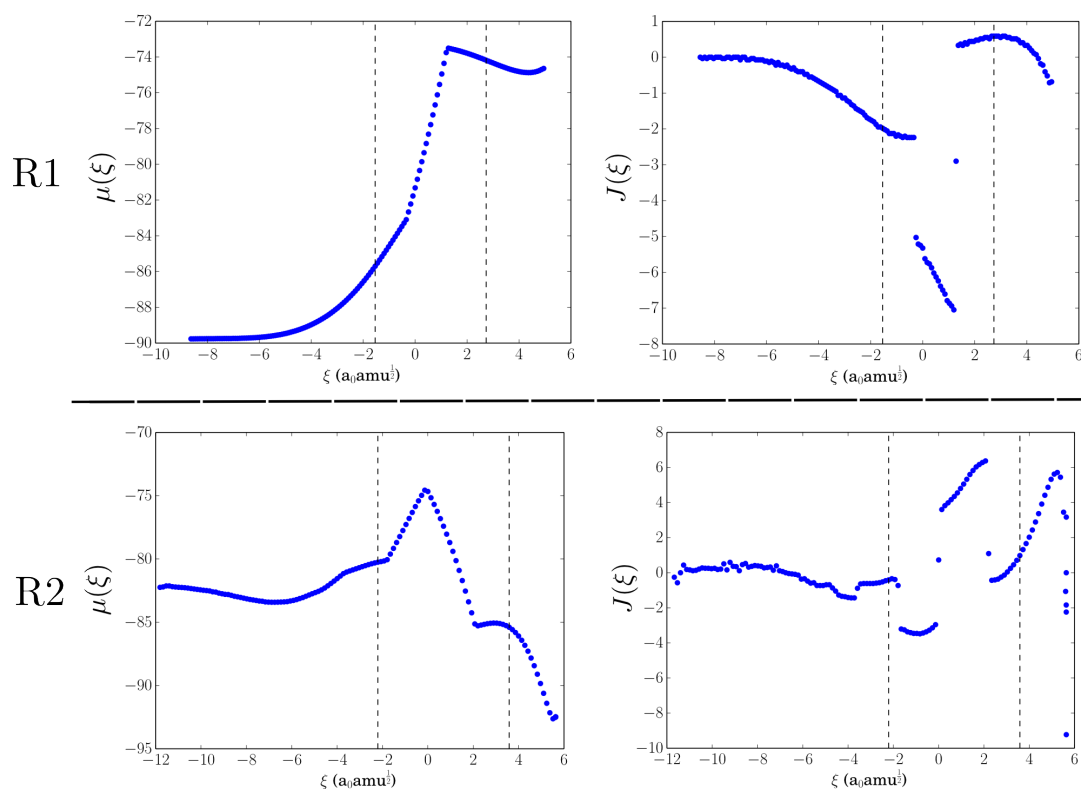


FIGURE F.2: Computed ill-defined chemical potential and reaction electronic flux for each reaction using orbital approximation.

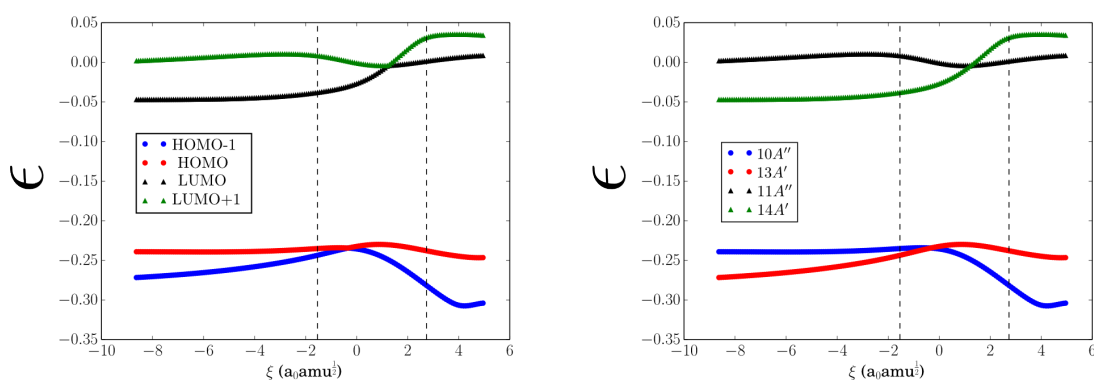


FIGURE F.3: Frontier molecular orbitals for **R1** in which is clearly depicted the orbital crossing (left). Symmetry-adapted orbitals for **R1** (right), note that orbital-crossing is avoided.

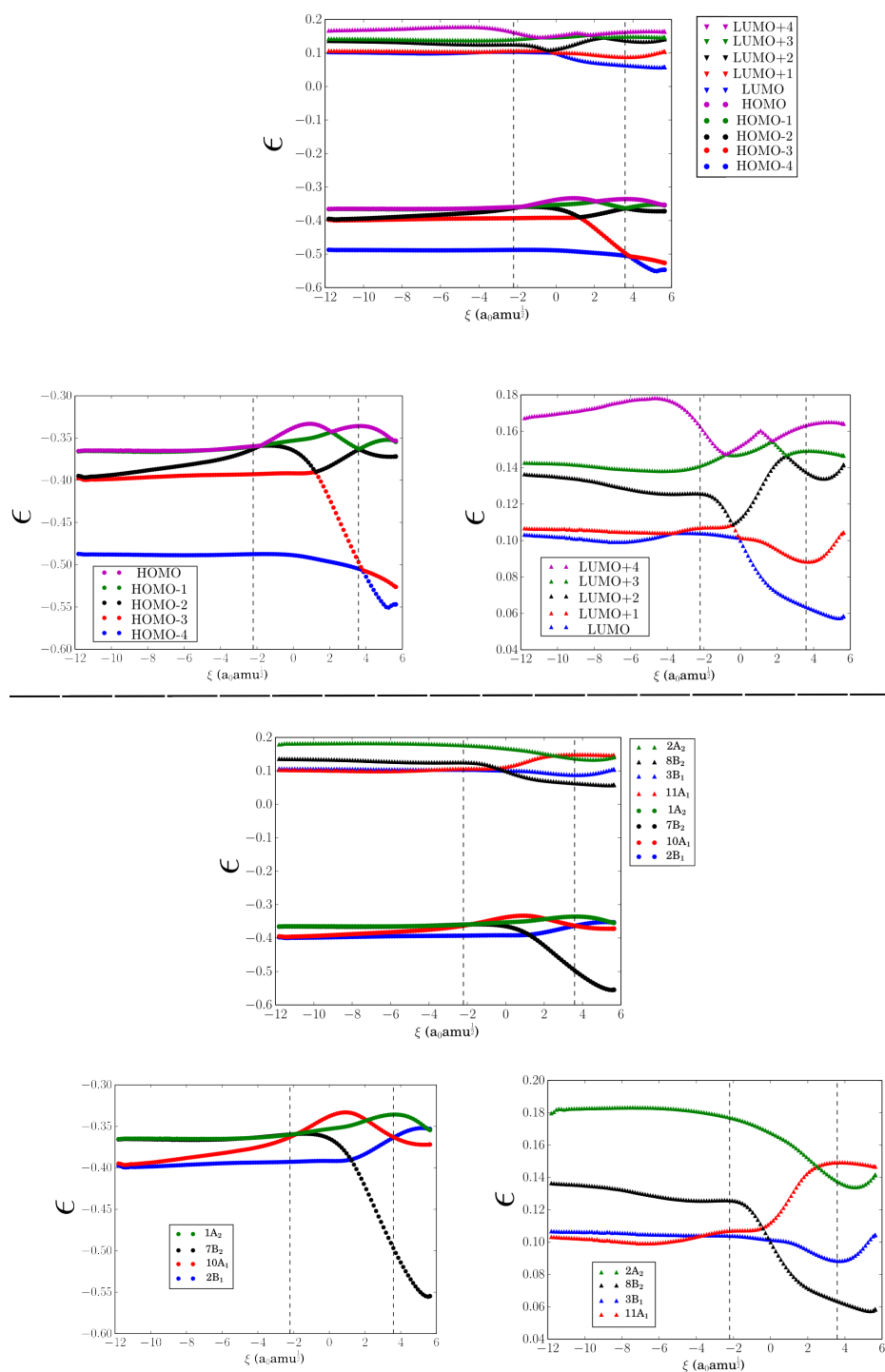


FIGURE F.4: Frontier molecular orbitals for **R2**, orbital crossings are more exhaustive due higher level of symmetry. Symmetry-adapted orbitals are depicted below.

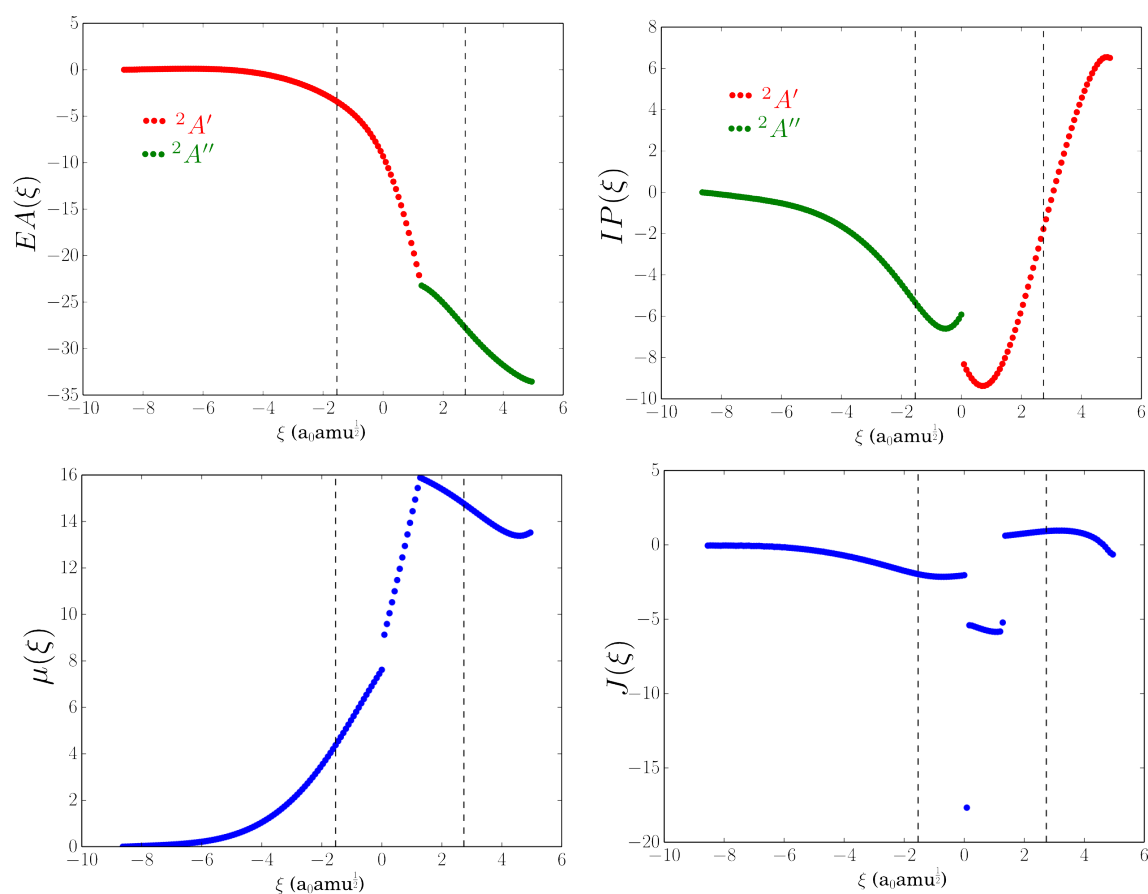


FIGURE F.5: Computed ill-defined chemical potential and reaction electronic flux using finite difference approximations are showed for **R1**. In $EA(\xi)$ and $IP(\xi)$ profiles, the electronic state of the anion and cation, respectively, are showed in color-code. Electronic state for the neutral system is found to be ${}^1A'$. Note that from the $EA(\xi)$ and $IP(\xi)$ profiles the multi-reference character showed as discontinuities is clearly observed.

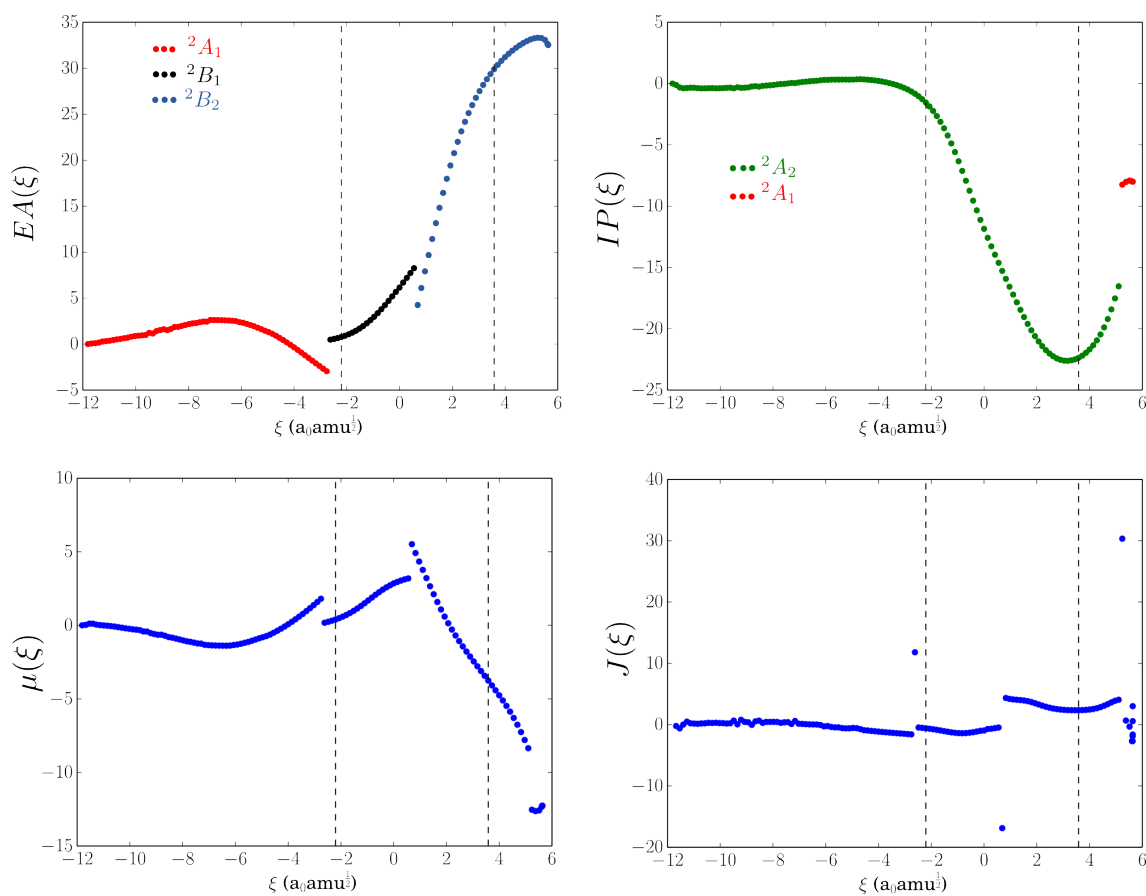


FIGURE F.6: Computed ill-defined chemical potential and reaction electronic flux using finite difference approximations are showed **R2**. In $EA(\xi)$ and $IP(\xi)$ profiles, the electronic state of the anion and cation, respectively, are showed in color-code. Electronic state for the neutral system is found to be 1A_1 . Note that from the $EA(\xi)$ and $IP(\xi)$ profiles the multi-reference character showed as discontinuities is clearly observed.

Appendix G

Energies for the Activation of H₂ by Aluminyll Anions

G.1 Activation Enthalpies

Reaction	$\Delta E_{\text{CBS}}^{\ddagger}$	$\Delta_{\text{ZPVE}}^{\ddagger}$	$\Delta_{\text{rel}}^{\ddagger}$	$\Delta_{\text{DBOC}}^{\ddagger}$	$\Delta_{\text{core}}^{\ddagger}$	$\sum \delta \Delta^{\ddagger}$	$\Delta H_{0K}^{\ddagger}$
Monosubstituted Aluminyll Anions							
AlHCH ₃ [−]	9.51	1.38	0.16	0.08	−0.22	1.41	10.92
AlHCN	11.06	1.26	0.22	0.09	−0.17	1.40	12.46
AlHNC [−]	14.65	1.11	0.22	0.06	−0.11	1.28	15.93
AlHNNH ₂ [−]	18.77	0.52	0.17	0.09	−0.09	0.69	19.46
AlHF [−]	17.42	0.69	0.19	0.07	−0.07	0.89	18.31
AlHOH [−]	18.63	0.35	0.18	0.09	−0.10	0.52	19.15
Disubstituted Aluminyll Anions							
AlH ₂ [−]	6.48	1.51	0.17	0.05	−0.04	1.69	8.17
Al(CH ₃) ₂ [−]	12.68	1.31	0.17	0.12	0.27	1.88	14.56
Al(CN) ₂ [−]	16.12	1.07	0.29	0.07	−0.14	1.30	17.42
Al(NC) ₂ [−]	26.06	0.75	0.32	0.09	0.04	1.20	27.26
Al(NH ₂) ₂ [−]	31.70	0.67	0.18	0.14	−0.02	0.97	32.67
Al(F) ₂ [−]	34.86	−0.44	0.25	0.10	0.18	0.10	34.96
Al(OH) ₂ [−]	31.97	−1.12	0.18	0.11	0.03	−0.80	31.17

TABLE G.1: Activation energies and different energy corrections. Energies are reported in kcal mol^{−1}.

G.2 Reaction Enthalpies

Reaction	$\Delta E_{\text{CBS}}^\circ$	$\Delta_{\text{ZPVE}}^\circ$	$\Delta_{\text{rel}}^\circ$	$\Delta_{\text{DBOC}}^\circ$	$\Delta_{\text{core}}^\circ$	$\sum \delta \Delta^\circ$	ΔH_{0K}°
Monosubstituted Aluminyll Anions							
AlHCH_3^-	-49.44	-4.69	0.42	0.04	0.81	-3.42	-52.86
AlHCN^-	-48.63	-4.43	0.29	0.08	1.05	-3.02	-51.65
AlHNC^-	-48.25	-4.22	0.30	0.04	1.08	-2.81	-51.06
AlHNH_2^-	-40.44	-4.54	0.23	0.06	0.94	-3.31	-43.75
AlHF^-	-46.27	-3.94	0.28	0.04	0.96	-2.65	-48.92
AlHOH^-	-42.81	-4.43	0.26	0.05	0.92	-3.20	-46.01
Disubstituted Aluminyll Anions							
AlH_2^-	-49.43	-4.53	0.25	0.02	0.94	-3.32	-52.75
$\text{Al}(\text{CH}_3)_2^-$	-49.19	-4.86	0.44	0.07	-0.04	-4.39	-53.58
$\text{Al}(\text{CN})_2^-$	-47.12	-4.45	0.33	0.06	1.30	-2.76	-49.88
$\text{Al}(\text{NC})_2^-$	-44.83	-4.04	0.36	0.07	1.36	-2.25	-47.08
$\text{Al}(\text{NH}_2)_2^-$	-33.94	-4.60	0.21	0.09	1.05	-3.25	-37.19
$\text{Al}(\text{F})_2^-$	-38.51	-3.26	0.33	0.07	1.16	-1.69	-40.20
$\text{Al}(\text{OH})_2^-$	-37.07	-3.13	0.29	0.08	1.08	-1.68	-38.75

TABLE G.2: Reaction energies and different energy corrections. Energies are reported in kcal mol⁻¹.

Appendix H

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APPLICATION OF LOW VALENT MAIN GROUP ELEMENTS IN SMALL MOLECULE ACTIVATION REACTIONS

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