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Prototropic and metallotropic migration of isolobal fragments on indol rings. Theoretical study and NBO analysis

S. jameh-Bozorghi [1]* , Z. Javanshir [1] & D. Nori-Shargh [1]
1Chemistry Department, Faculty of science, Arak Branch, Islamic Azad University, Arak, Iran
e-mail: Sjamehbozorgi@gmail.com

ABSTRACT

Molecular structures, energies, NBO analysis and sigmatropic behaviour of 1-Indenyl(dihydro)borane (**1**) and 1-Indenyl-threecarbonylcobalt(I) (**2**) were investigated using DFT and *ab initio* molecular orbital methods. In these compounds BH_2 and $Co(CO)_3$ fragments are isolobal. The Results of calculations using *B₃LYP*, HF and MP2 methods [Basis set 6-311+G**] showed that $-BH_2$ and $-Co(CO)_3$ had similar behaviour in sigmatropic shifts. Prototropic shifts in compounds **1** and **2** have similar mechanisms too. Results showed that metallotrotropic shift is faster than Prototrpic shift in compounds **1** and **2**. The activation energies (Ea) of Prototropic shift in compounds **1** and **2** are 18.83 and 17.38 $kcal.mol^{-1}$. These energies are higher than $-BH_2$ shifts in compound **1** (10.11 $kcal.mol^{-1}$) or migration of $-Co(CO)_3$ fragment in compound **2** (12.39 $kcal.mol^{-1}$). Lower amount of activation energy in borotropic shift and cobalt`s fragment shift show that rotation of boron and cobalt on the indol ring can happen in the ambient temperature. Calculation results revealed that migration of proton and $Co(CO)_3$ was carried out via suprafacial[1,2]-sigmatropic mechanism while $-BH_2$ shift took place via antrafacial [1,3]-rearangment.

Keywords

Ab initio; Isolobal; indol; sigmatropy; metallotropic; prototropic.

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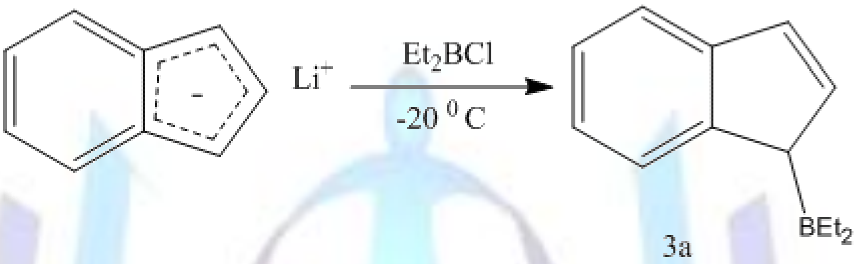
INTRODUCTION

Fluxional σ-cyclopentadienyl compounds such as $(\eta^1\text{-}C_5H_5)_2Hg$ and $(\eta^5\text{-} C_5H_5)$ $(\eta^1\text{-}C_5H_5)Fe(CO)_2$ were first discovered by Piper and Wilkinson in 1965[1]. The 1,2-migration of carbon-group elements in cyclopentadienyl compounds was first experimentally discussed by Fritz and Kreiter for silicon-, germanium-, tin-substituted cyclopentadienes [2,3]. *Ab initio* study of behaviours, metallotropic 1,2-shift and prototropic 1,2-shift of cyclopentadienyl(trimethyl)-Silane, -German and –Stannane were carried out by Nori-shargh *et-al* in 2003. In this research calculation results showed that allylic isomer is the most stable isomer of the mentioned compounds. Also, it was revealed that prototropic shift is much slower than metallotropic shift [4]. Gridnev and Meller investigated fluxional behaviour of 1- Indenyl(dihydro)borane in 1998 [5]. The authors discussed in a non-detailed but essentially correct manner why fast intra-molecular 1,2-migrations of the metal moiety around the 1-Indenyl ring occur. The order of relative thermodynamic stability of triorganoboranes nicely corresponds to the known order for the corresponding hydrocarbons [6].

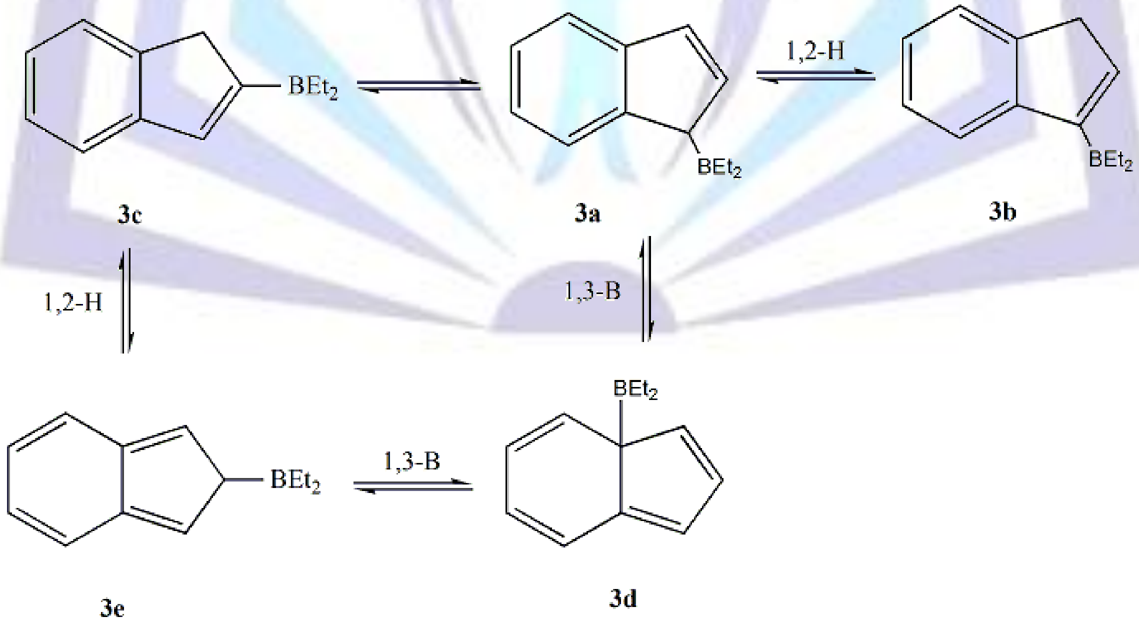
Fluxional 1-indenyl(diethyl)borane (**3a)** was prepared from indenyllithium and diethylboron chloride in hexane [7]. (Scheme 1)



Scheme 1: Preparation of 1-indenyl(diethyl)borane

NMR spectra of borane **3a** was taken in the temperature interval 25–80 °C and three cross-peaks corresponding to the migrations of the diethylboryl group from position 1 to position 3 were found [7].

A sigmatropic migration of hydrogen takes place at elevated temperatures in **3a**. This leads to the establishment of a dynamic equilibrium between the three isomers **3a**, **3b**, and **3c** (Scheme 2). A small amount (about 6 %) of 2-indenyl (diethyl) borane **3c** apparently appears by a [1,2]-H shift in the *iso*-indenyl intermediate **3e**, which is formed from **3a** via two consequent [1,3]-B shifts [7].



Scheme 2: sigmatropic migration of hydrogen and boron

Sigmatropic migration of many fragments on aromatic rings has been observed. These compounds are fluxional. Experimental [1] and theoretical [4] studies on barrier energies and rate of (σ)metallotropic and (σ)prototropic shift on Fluxional compounds were carried out.

1H-NMR, 13C-NMR, mass spectrometer and IR studies of the structures of *1-Indenyl(dihydro)borane* indicated that the isomer 3 is the most stable isomer. In solution state, four compounds have been found to undergo rapid metallotropic shifts much faster than prototropic shifts which give allylic nonfluxional isomers [8-15].

The isolobal principle has been devised by Roald Hoffmannin in *Organometallic Chemistry* [16]. The methyl radical is isolobal with the metal carbonyl species manganese pentacarbonyl $Mn(CO)_5$ because both molecules have a single electron in a hybrid orbital pointing away from the plane of the molecule (though they are not isoelectronic). This resemblance is reflected in the chemistry of both molecules. As the methyl radical can dimerize to ethane, $Mn(CO)_5$ can dimerize to $(CO)_5Mn\text{-}Mn(CO)_5$ and both radicals can form $Mn(CO)_5CH_3$. So, it can be inferred that $-BH_2$ and $-Co(CO)_3$ are isolobal groups. Those were showed their HOMO and LUMO diagram in fig 1.

As the above mentioned, fluxional behaviour of boron in indenyl(dihydro)boran observed [5], but mechanism of this behaviour was not investigated. On the other hand, any experimental or theoretical investigation about structural, fluxional behaviour and sigmatropic shifts mechanism of isolobal compound with indenyl(dihydro)boran not performed.

The main goal of this work is investigation of sigmatropic behaviour of indenyl(dihydro)boran. Also, presentation, investigation of structural and fluxional properties and sigmatropic shifts mechanism for inorganic isolobal compound with indenyl(dihydro)boran and comparison together.

Calculation were performed by *ab initio* molecular orbital (MO) and hybrid density functional theory (hybrid-DFT: *B3LYP*/6-311+G** based method using the GAUSSIAN 2003 package of programs and NBO 3.1 [17-21].

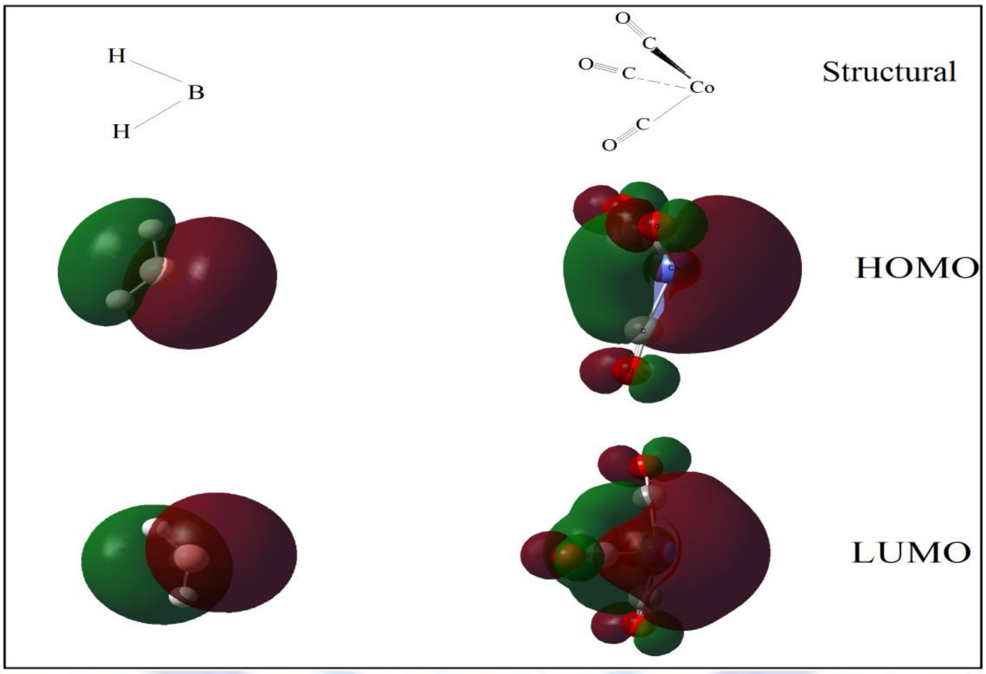
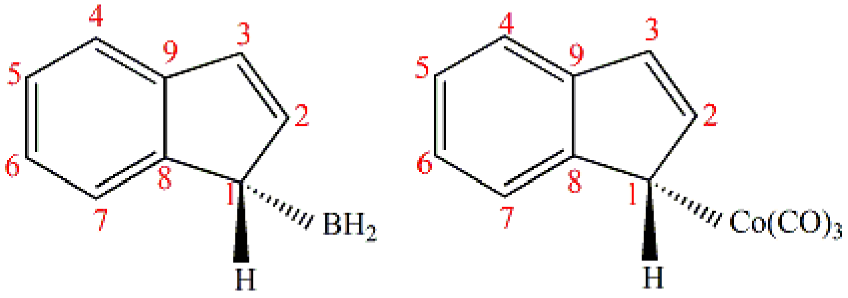


Figure 1:Similarity of HOMO and LUMO diagrams for optimized structure of BH_2 and $[Co(CO)_3]$

The nature of the stationary points for compounds has been determined by virtue of the number of imaginary frequencies. For minimum state structures, only real frequency values, and in the transition state only single imaginary frequency values (with a negative sign) are accepted.



1

2

Scheme 3: Structure of compounds 1 and 2

CALCULATION DETAILS

Ab initio molecular orbital (MO) calculations were carried out using *B3LYP*/6-311+G** level of theory with the GAUSSIAN 2003 package of programs [21] on a personal computer.

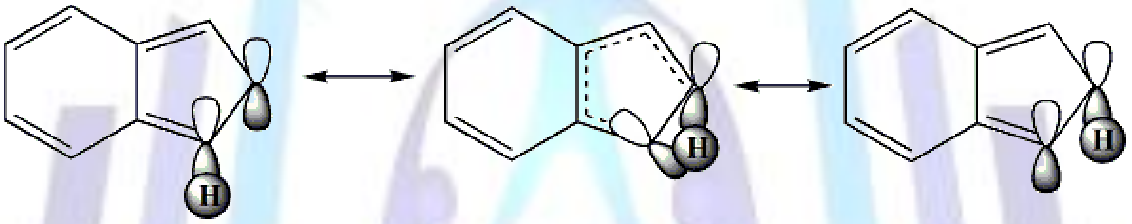
Vibrational frequency amounts for all ground and transition state structures were calculated at *B3LYP*/6-311+G** level of theory for compound **1**, but for compound **2,** due to their large size, they were calculated at *B3LYP*/lanl2dz level of theory.

The Basis series and method dependencies were probed by single point energies computed at *B3LYP*/6-311+G**, HF/6-311+G**, MP2/6-311+G** optimized geometries.

Energy-minimum molecular geometries were located by minimizing energy with respect to all geometrical coordinates without imposing any structurally symmetrical constraints and transition state structures were obtained by QST2 subroutine. [22, 23] Natural Bond Orbital (NBO) analysis was then performed at the *B3LYP*/6-311+G** level by the NBO 3.1 program included in the GAUSSIAN 03 package of programs.

RESULT AND DISCUSSION

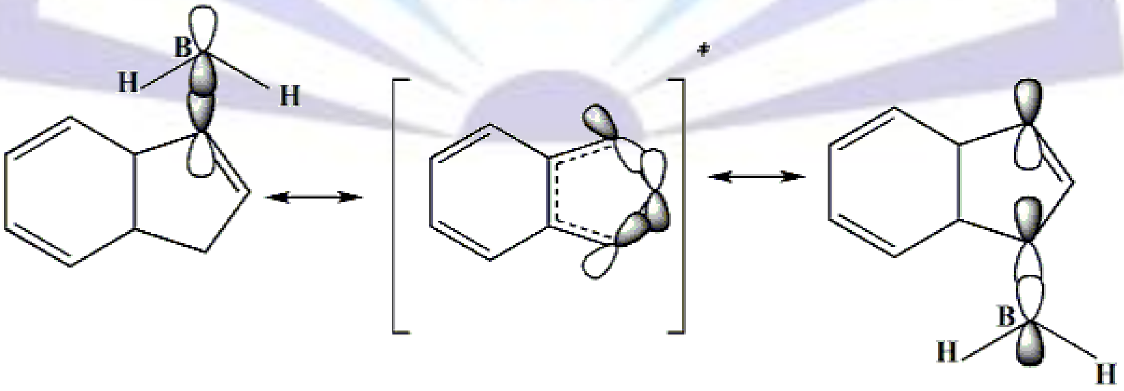
Structural properties, energies behaviour and NBO analysis were investigated using *ab initio* molecular orbital (MO) and hybrid density functional theory (hybrid-DFT: *B3LYP*/6-311+G**) for compounds **1** and **2**. In these two compounds [1,2] hydrogen shifts occur by a symmetry-allowed suprafacial rearrangement, as illustrated in scheme 4. Contrary to [1,2] sigmatropic hydrogen shift, however, thermal [2,3] hydrogen shifts are unknown**.**



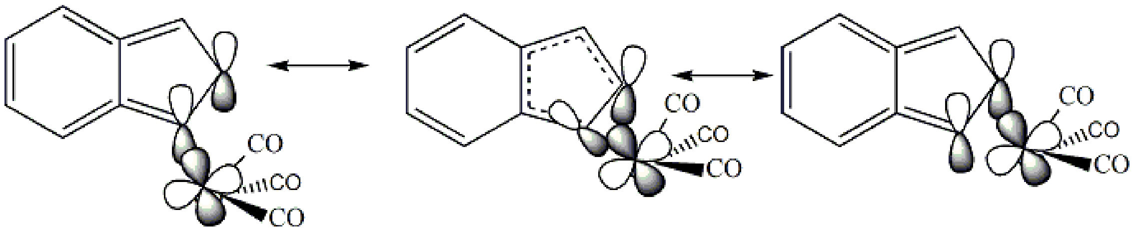
Scheme 4 : symmetry-allowed suprafacial [1,2] rearrangement of proton

BH_2 shifts cannot occur through [1,2] superafacial rearrangement. This migration is a [1,3] antrafacial rearrangement (scheme 5), But $Co(CO)_3$ shifts can occur through [1,2] superafacial rearrangement as illustrate in (scheme 6). In compounds **1** and **2** prototropic 1,2-shifts hydrogen migration occurred stepwise from C(1) to C(2) and from C(2) to C(3). Also, in compound **2** the $Co(CO)_3$ fragment migration occurred stepwise from C(1) to C(2) and from C(2) to C(3) similar hydrogen shift (see Figures 3 and 4). But in compound **1** -BH_2 fragment migration did not occur from C(1) to C(2); it only occurred from C(1) to C(3) through [1,3].

HOMO diagram of transition state structure of compounds **1** and **2** are shown in fig 2. In HOMO diagram of compound **1** one node is exist on C(2) atom, then sigmatropic shift from C(1) to C(2) is impossible, but suitable overlap of frontier orbitals of BH_2 with C(1) and C(3) produce a [1,3]-sigmatropic shift of BH_2 (see fig 2). On the other hand HOMO diagram of compound **2** showed that suitable overlap of orbitals for [1,2]-sigmatropic shift of $Co(CO)_3$ fragment is appear and not node on C(2) of C_5H_5 ring . Therefore 1,2-metallotropic shift would be occurred.



Scheme 5 : [1,3] antrafacial rearrangement of BH_2 fragment



Scheme 6 : [1,3] symmetry-allowed suprafacial [1,2] rearrangement of Co(CO)$_3$

When BH$_2$ is in vinylic position these compounds are not in ground state. Infra Red (IR) vibration frequencies (an imaginary frequency) and Aromatic Stabilization Energy (ASE = 3.62 Kcal.mol-1) as well as bond lengths of C-B that increased to 1.69 Angstrom results showed that this structure is a transition state one (fig. 3 and table 1). Also IRC calculation confirmed that BH$_2$ in vinylic position is a transition structure (fig.5).

Prototropic and metallotropic shift pathways of compounds **1** and **2** are shown in Figures 3 and 4, respectively.

Structural parameters, total electronic (E_{el}) energy, corrected zero point (ZPE^c) energies of compounds **1** and **2**, calculated on the *ab initio* and DFT levels of theory are given in Tables 1–7. The migration mechanisms for the BH$_2$, Co(CO)$_3$ and hydrogen were also investigated and structure of ground states and transition states of all compounds were investigated. Calculated results revealed that Indol rings are planar in the ground state and non planar in transition state for compounds **1** and **2**. δ_{1239} and δ_{2398} values are 0.0000 for ground state of compounds **1** and **2** while these values are 16.34 and -10.04 for compound **1** and -3.05 and 2.56 for compound **2**, respectively(see table 1 and 4)

Also, reaction pathways were shown in Figures 3 and 4. In metallotropic 1,2-shifts, the reaction pathways are symmetrical and in the transition state structure, the BH$_2$, Co(CO)$_3$ groups are equidistant from two carbon atoms of the C_9H_7 rings (see Tables 1 and 4). According to the results, comparing C-B and C- Co shows an increase in bond lengths while in the contrary, the dissociation of a C-B bond is easier than that of a C-Co bond which in turn, leads to the migration of the metal around the indol ring with a lower energy barrier. This result is in good agreement with the mentioned experimental data.

As it can be inferred from the Figures 3 and 4 the prototropic 1,2-shifts require higher energy barrier than metallotropic 1,2-shifts, consequently, the rate of this process is much slower than that of metal migration.

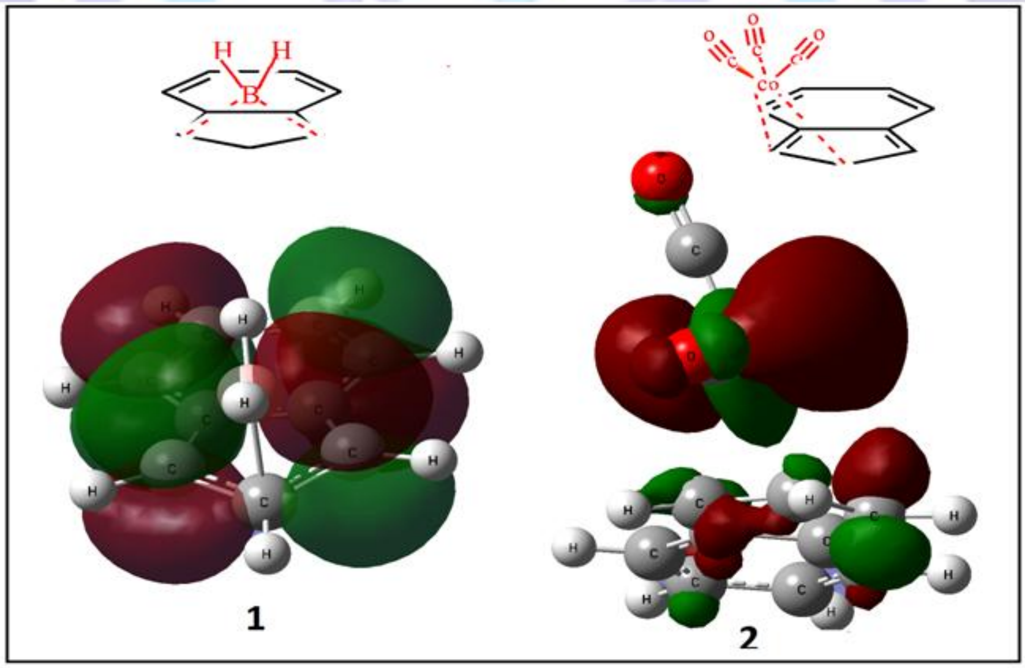


Figure 2: HOMO diagram of optimized metallotropic transition state structural of compound 1, 2

Ab initio and DFT calculation results showed that the energy barrier of prototropic shift in compound 1 and 2 from C(1) to C(2) is equal to the prototropic shift from C(2) to C(3) (see table 1). Calculation results revealed that BH$_2$ [1,2] migration need 10.11 kcal.mol^{-1} that is a lower migration energy comparing to Co(CO)$_3$ (12.39 kcal.mol-1) while bond lengths of C-B and C-Co are 1.562 and 2.082 Angstrom. On the other hand NBO calculation results showed that electron occupancies of C1 –B bond is 1.9 while occupancies of. C1 – Co bond is 1.74. The mentioned results concluded that C-Co bond has an irregular strength. The reason for straight of C-Co bond and the higher level of the barrier energy for Co(CO)$_3$ migration is related to the existence of a π back bonding between Co and C. *B3LYP*/6-311+G** results showed that the prototropic shift barrier energy for compound 1 is 30.4 Kcal mol-1 and for compound 2 is 50.3Kcal mol-1. Therefore, it was revealed that prototropic shifts for compound 1 have lower migration energy comparing to compound 2. It can be concluded that the prototropic 1,2-shifts occur only at higher temperatures. These results have a good agreement with structural and NBO results.

CONCLUSIONS

The calculation results at *B3LYP*/6-311+G**, HF/6-311+G** and MP2/6-311+G** levels of theory show that the most stable isomers of compounds **1** and **2** are the allylic isomers.

BH_2 shift in compound **1** cannot occurred via [1,2] migration and performed via [1,3] sigmatropic shift because compound **1** has one node on C(2) atom in HOMO diagram while in compound **2** this migration occurred at [1,2]-metallotropic shift because HOMO diagram of this compound showed suitable overlap of orbitals for [1,2]-sigmatropic shift of $Co(CO)_3$ fragment. In a similar vein, the occurrence of [1,2]-prototrophic shift for the two compounds was easy.

Bond legth of Co-C is longer than B-C and electronic occupancies of Co-C is lower than B-C while sigmatropic barrier energy for $Co(CO)_3$ migration is higher than BH_2 migration, because Co-C bond has a π-back bonding which makes it stronger than B-C.

Barrier height of metalotropic shift is lower than prototrophic shift. Lower amount of activation energy in borotropic shift and cobalt`s fragment shift show that rotation of boron and cobalt on the indol ring can happen in the ambient temperature, but prototropic migration occurred at higher temperature.

Table 1. DFT/6-311+G Calculated Structural Parameters and Energies of the Ground States and TransitionStates of 1-indenyl(dihydro)borane (1).. Bond Lengths are in Angstrom Units (Å) and Angles in Degrees (º)**

Compounds	**1**	**2**	**3**	**1→2**	**2→3**	**1→1′**
Bond lengths						
B- C_1	1.56273	1.51033	1.53260	1.51066	1.50681	----
B-C_2	---	---	---	---	---	1.69025
C_1- C_2	1.51135	1.51257	1.36365	1.52426	1.43488	1.42411
C_2- C_3	1.34642	1.48755	1.50246	1.39680	1.46514	1.42408
C_3- C_9	1.46326	1.36747	1.51020	1.41786	1.42143	1.45149
C_1- C_8	1.51212	1.39362	1.48322	1.44162	1.43745	1.45151
C_3- H_2	1.08277	1.08283	1.09811	1.08114	1.08147	1.08004
C_1- H_1	1.11591	---	---	1.36322	---	1.08003
C_2- H_1	---	1.10046	---	1.25449	1.26195	---
C_3- H_1	---	---	1.09811	---	1.39146	---
Occupancy						
B- C_1	δ=1.94532	δ=1.97749	δ=1.97686	δ=1.97792	δ=1.97432	---
B-C_2	---	---	---	---	---	---
C_1- C_2	δ=1.97204	δ=1.97433	δ=1.98051 π=1.79633	δ=1.90469	δ=1.97620	δ=1.95676
C_2- C_3	δ=1.98112 π=1.90399	δ=1.98029	δ=1.98053	δ=1.98158	δ=1.94330	δ=1.96830 π=1.52963
C_3- C_9	δ=1.97299	δ=1.97933 π=1.74179	δ=1.97656	δ=1.97492 π=1.58434	δ=1.97743 π=1.56231	δ=1.97352
C_1- C_8	δ=1.97093	δ=1.97523 π=1.69034	δ=1.96873	δ=1.97261 π=1.54679	δ=1.97013 π=1.58574	δ=1.97372
C_3- H_2	δ=1.98282	δ=1.98490	δ=1.95046	δ=1.98244	δ=1.98579	δ=1.98182
C_1- H_1	δ=1.88938	---	---	---	---	δ=1.98362
C_2- H_1	---	δ=1.93470	---	δ=1.54270	δ=1.53881	---

C_3- H_1	---	---	δ=1.95046	---	---	---
Bond angles(°)						
$B-C_1-C_2$	118.02271	125.90587	123.34432	124.92483	124.70329	56.90268
$B-C_1-C_8$	119.93351	128.04433	129.36956	131.34540	129.72983	---
$B- C_2-C_3$	---	---	---	---	---	78.20513
$C_1-C_2-C_3$	110.62816	105.72514	112.22000	108.75079	109.36508	107.58036
$C_2-C_3-C_9$	109.72225	109.17748	102.59078	108.94560	106.98556	107.32653
$C_3-C_9-C_8$	108.33501	108.52808	108.73209	108.80419	107.75667	107.50909
$C_9-C_8-C_1$	108.51049	110.51950	109.17101	109.74990	110.30320	107.50903
$C_8-C_1-C_2$	102.77879	106.04980	107.28612	103.70446	105.56395	107.32504
Torsion angles(°)						
$B-C_1-C_2-C_3$	132.84495	-179.99577	-179.99263	176.18452	178.54898	73.42660
$B- C_2-C_3-C_9$	---	---	---	---	---	89.77101
$C_1-C_2-C_3-C_9$	1.21045	-0.00397	0.00000	1.73259	1.55087	16.34794
$C_2-C_3-C_9-C_8$	-0.25985	0.00000	0.00000	-0.60049	-1.58258	-10.04310
$C_8-C_1-C_2-C_3$	-1.60868	0.00385	0.00000	-2.16235	-0.87733	-16.34587
ZPE^c	0.1407435	0.13641949	0.1418039	0.1381100	0.138373	0.142049
*E*el	-373.286206	-373.273922	-373.297751	-373.245477	-373.245865	-373.27141
E_a= *E*el + *ZPE*^{c}	-373.145462	-373.137502	-373.155947	-373.107366	-373.1074915	-373.129360
$\Delta E^b{}_a$(Hartree)	0.010485	0.018445	0.00	0.048581	0.048455	0.026587
ΔE_a(kcal mol^{-1})	6.57	11.57	0.00	30.48	30.405	16.68
$E^c{}_a$(kcal mol^{-1})				23.91	18.83	10.11
ΔH				5.00	-11.57	0.00

[a] Corrected by multiplying by a scaling factor (0.9409).

[b] Relative to the most stable structure

Table2. HF/6-311+G Calculated Single Point Structural Parameters and Energies of the Ground States and Transition States of 1-indenyl(dihydro)borane**

Compounds	**1**	**2**	**3**	**1→2**	**2→3**	**1→1′**
ZPE^a	0.1407435	0.13641949	0.1418039	0.1381100	0.138373	0.142049
*E*el	-370.7891546	-370.7666385	-370.8010636	-370.7269038	-370.731217	-370.7508864
E_a= *E*el + *ZPE*	-370.648411	-370.6302190	-370.6592597	-370.5887938	-370.592844	-370.6088374
$\Delta E^b{}_a$(Hartree)	0.0108487	0.0290407	0.00	0.0704659	0.0664157	0.0504223
ΔE_a(kcal mol^{-1})	6.80	18.22	0.00	44.21	41.67	31.63
$E^c{}_a$(kcal mol^{-1})				37.41	23.45	24.83
ΔH				11.42	-18.22	0.00

Table 3. MP2/6-311+G** Calculated Single Point Structural Parameters and Energies of the Ground States and Transition States of 1-indenyl(dihydro)borane

Compounds	1	2	3	1→2	2→3	1→1′
ZPE	0.1407435	0.13641949	0.1418039	0.1381100	0.138373	0.142049
Eel	-372.1147183	-372.0951642	-372.1245096	-372.0754224	-372.0732901	-372.104577
E_a= Eel + ZPE	-371.9739748	-371.9587447	-371.9827057	-371.9373124	-371.9349171	-371.962528
ΔE^b_a(Hartree)	0.0087309	0.023961	0.00	0.045393	0.047788	0.0201777
ΔE_a(kcal mol^{-1})	5.47	15.03	0.00	28.48	29.98	12.66
E^c_a(kcal mol^{-1})				17.43	14.95	7.19
ΔH				9.56	-15.03	0.00

Table 4. *B3LYP*/lanl2dz Calculated Structural Parameters and Energies of the Ground States and TransitionStates of -indenyl(tricarbonyl)cobalt..Bond Lengths are in Angstrom Units (Å) and Angles in Degrees (º)

Compounds	1	2	3	1′	1→2	2→3	1→1′
Bond lengths							
Co- C_1	2.0823	1.9687	1.97477	----	1.9738	1.9729	2.2281
Co-C_2	---	---	---	2.0581	---	----	2.1700
C_1- C_2	1.4925	1.5288	1.3680	1.4386	1.5195	1.4349	1.4561
C_2- C_3	1.3735	1.5153	1.5263	1.4386	1.4265	1.51227	1.4465
C_3- C_9	1.4679	1.3759	1.5193	1.4869	1.4195	1.4239	1.4224
C_1- C_8	1.47509	1.3869	1.4871	1.4869	1.4426	1.4321	1.4462
C_3- H_2	1.083	1.0845	1.1010	1.0840	1.0826	1.0824	1.0836
C_1- H_1	1.086	---	---	1.0840	1.4102	---	1.0839
C_2- H_1	---	1.1023	---	1.0810	1.2882	1. 2822	1.0848
C_3- H_1	---	---	1.1010	---	----	1.4112	----
Occupancy							
Co- C_1	δ=1.72311	δ=1.74311	δ=1.75148	δ=1.63217	δ= 1.78323	1.74890	-----
Co-C_2	---	---	---	---	---	---	---
C_1- C_2	δ=1.97509	δ=1.97008	δ=1.97911	δ=1.97372	δ= 1.92836	δ= 1.97547	δ= 1.96837
			π=1.87147				
C_2- C_3	δ=1.98003	δ=1.97182	δ=1.96906	δ=1.97453	δ= 1.97599	δ= 1.93681	δ= 1.97695
	π= =1.86540			π= =1.61057	π= = 1.67259		
C_3- C_9	δ=1.97187	δ=1.97970	δ=1.97430	δ=1.97258	δ= 1.97472	δ= 1.97727	δ= 1.97383
		π=1.81127				π= 1.62918	π= 1.62762
C_1- C_8	δ=1.96700	δ=1.97588	δ=1.96729	δ=1.97194	δ= 1.97292	δ= 1.97064	δ= 1.97326
		π=1.76281			π= 1.59625	π= 1.63203	π= 1.60305
C_3- H_2	δ=1.98064	δ=1.98053	δ=1.95430	δ=1.98174	δ= 1.97890	δ= 1.98197	
C_1- H_1	δ=1.97173	---	---	δ=1.98086	---	-----	δ= 1.97727
C_2- H_1	---	δ=1.94217	---	-----	δ= 1.97930	δ= 1.97854	δ= 1.97695
C_3- H_1	---	---	δ=1.95401	---	----	---	δ= 1.98191

Bond angles(°)							
Co-C_1-C_2	117.265	122.795	128.815	63.857	127.788	125.596	68.523
Co-C_1-C_8	76.578	129.727	122.737	99.828	127.097	127.393	111.353
Co- C_2-C_3	---	---	---	---	---		108.748
C_1-C_2-C_3	110.393	104.824	111.424	106.305	109.023	108.524	118.467
C_2-C_3-C_9	108.721	108.692	102.551	107.766	108.037	106.091	108.185
C_3-C_9-C_8	107.730	109.234	108.924	107.029	109.215	108.446	108.179
C_9-C_8-C_1	108.176	109.769	108.652	107.031	119.332	109.886	108.363
C_8-C_1-C_2	104.765	107.477	108.447	107.769	104.336	107.009	106.718
Torsion angles(°)							
Co-C_1-C_2-C_3	-79.222	179.796	179.988	----	-168.039	177.880	-104.565
Co- C_2-C_3-C_9	---	---	---	92.334	---	-----	-80.622
C_1-C_2-C_3-C_9	-0.3962	0.0314	0.00000	19.870	-1.6289	2.1033	-3.0516
C_2-C_3-C_9-C_8	-2.5393	-0.0042	0.0109	-12.313	0.2636	-1.4509	2.5691
C_8-C_1-C_2-C_3	3.0747	-0.0482	-0.0107	-19.866	2.3406	-1.9063	2.3156
ZPE^c	0.145825	0.144513	0.145733	0.146057	0.144425	0.141616	0.145364
Eel	-832.1312	-832.0846	-832.1186	-832.1274	-832.0491	-832.0484	-832.1064
E_a= Eel + ZPE	-831.985375	-831.940087	-831.972867	-831.981343	-831.904675	-831.906784	-831.961036
$\Delta E^b{}_a$(Hartree)	0.00	0.045288	0.012508	0.004032	0.0807	0.078591	0.024339
ΔE_a(kcal mol^{-1})	0.00	28.41	7.84	2.53	50.63	49.31	15.27
$E^c{}_a$(kcal mol-1)					50.63	20.9	15.27
ΔH					28.36	-20.92	2.56

[a] Corrected by multiplying by a scaling factor (0.9409).

[b] Relative to the most stable structure

Table 5. *B3LYP*/6-311+G Calculated Single Point Structural Parameters and Energies of the Ground States and Transition States of 1-indenyl(tricarbonyl)cobalt**

Compounds	**1**	**2**	**3**	**1′**	**1→2**	**2→3**	**1→1′**
ZPE^a	0.145825	0.144513	0.145733	0.146057	0.144425	0.141616	0.145364
Eel	-2070.1316	-2070.0852	-2070.1200	-2070.1376	-2070.0648	-2070.0546	-2070.1114
E_a= Eel + ZPE	-2069.98577	-2069.94068	-2069.97426	-2069.99154	-2069.91138	-2069.91298	-2069.96603
$\Delta E^b{}_a$(Hartree)	0.005768	0.050856	0.017276	0.00	0.0801593	0.078559	0.025507
ΔE_a(kcal mol^{-1})	3.61	31.91	10.84	0.00	50.3	49.29	16.00
$E^c{}_a$(kcal mol^{-1})					46.69	17.38	12.39
ΔH					28.24	-21.03	-3.61

Taable 6. HF/6-311+G Calculated Single Point Structural Parameters and Energies of the Ground States and Transition States of 1-indenyl(tricarbonyl)cobalt**

Compounds	**1**	**2**	**3**	**1′**	**1→2**	**2→3**	**1→1′**
ZPE^a	0.145825	0.144513	0.145733	0.146057	0.144425	0.141616	0.145364
*E*el	-2064.37293	-2064.33268	-2064.3760	-2064.37035	-2064.30028	-2064.29053	-2064.36544
E_a= Eel + *ZPE*	-2064.22710	-2064.18816	-2064.2303	-2064.2243	-2064.15586	-2064.14891	-2064.22008
ΔE^b_a(Hartree)	0.003204	0.0421422	0.00	0.006011	0.074449	0.0813928	0.01023
ΔE_a(kcal mol^{-1})	2.01	26.44	0.00	3.77	46.71	51.07	6.41
E^c_a(kcal mol^{-1})					44.70	24.63	4.40
ΔH					24.38	-26.39	1.76

Table 7. MP2/6-311+G Calculated Single Point Structural Parameters and Energies of the Ground States and Transition States of 1-indenyl(tricarbonyl)cobalt**

Compounds	**1**	**2**	**3**	**1′**	**1→2**	**2→3**	**1→1′**
ZPE^a	0.145825	0.144513	0.145733	0.146057	0.144425	0.141616	0.145364
*E*el	-2067.13836	-2067.07733	-2067.11572	-2067.158092	-2067.05239	-2067.05414	-2067.11326
E_a= Eel + *ZPE*	-2066.99253	-2066.93282	-2066.96998	-2067.012035	-2066.90796	-2066.91252	-2066.96790
ΔE^b_a(Hartree)	0.019498	0.0792324	0.0420466	0.00	0.1040694	0.0995078	0.0441299
ΔE_a(kcal mol^{-1})	12.23	49.71	26.38	0.00	65.30	62.44	27.69
E^c_a(kcal mol^{-1})					53.07	12.73	15.46
ΔH					37.48	-23.33	-12.23

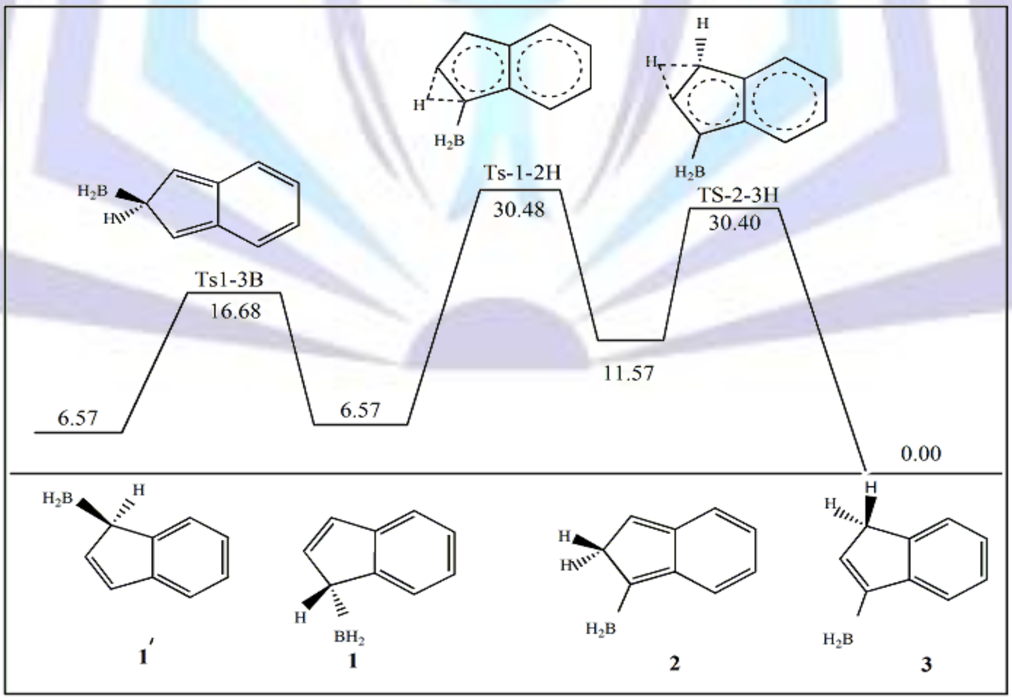


Figure 3: ***B3LYP*/6-311+G** energy diagram for various sigmatropic shifts in compound 1**

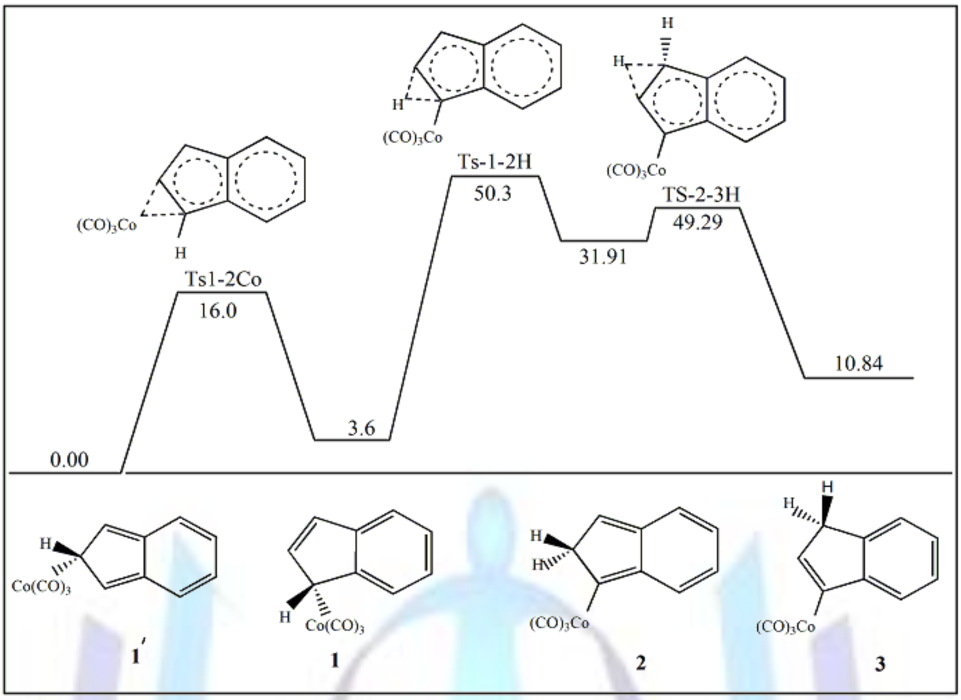


Figure 4: ***B3LYP**/**6-311+G** energy diagram for various sigmatropic shifts in compound 2**

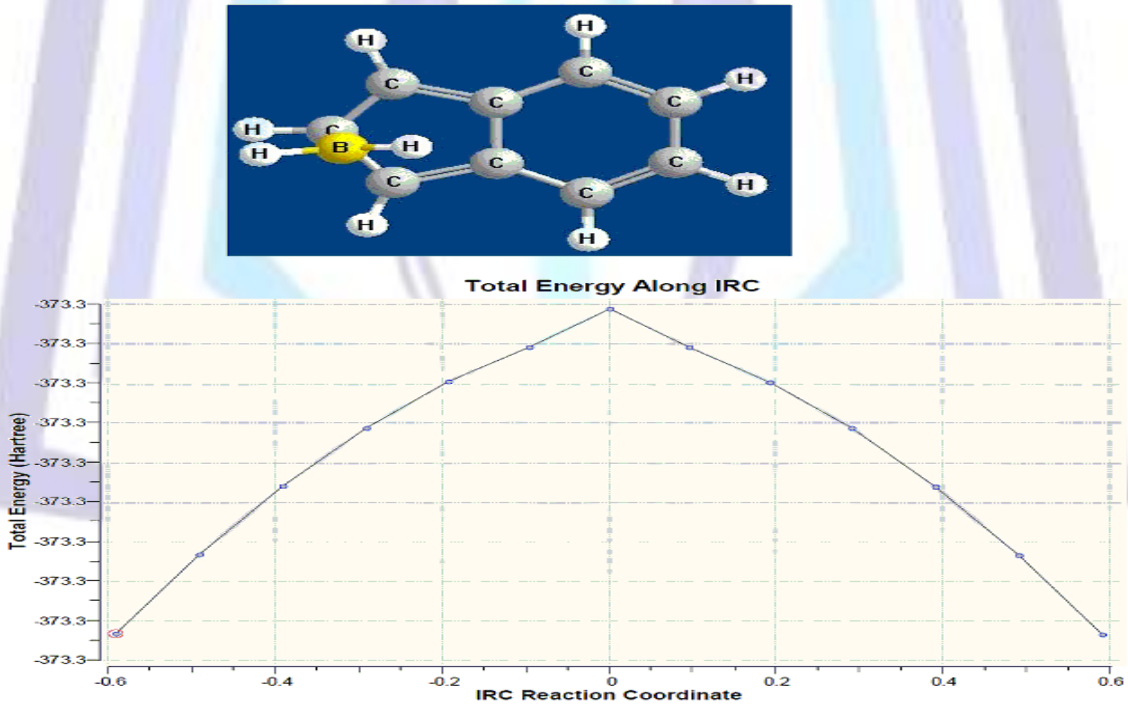


Figure 5: IRC plot of [1,3] shift for borotropic compound 1

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