

Ab initio and DFT study of prototropic and metallotropic 1,5-shifts of isolobal cyclopentadienyl derivatives

Zahra Javanshir¹, Saeed Jameh-Bozorgi^{2,*} and Ali-reza Namdari³

¹Department of Chemistry, Faculty of Sciences, Ahar Branch, Islamic Azad University, Ahar, Iran

²Department of Chemistry, Faculty of Sciences, Hamadan Branch, Islamic Azad University, Hamadan, Iran

³Department of Chemistry, Faculty of Sciences, Shahr-e-Rey Branch, Islamic Azad University, Shahr-e-Rey, Iran

The structures, energies and sigmatropic behaviour of η^1 -cyclopenta-2,4-dienylborane (1) and η^1 -cyclopentadiene-three carbonyl cobalt (I) (2) were examined using DFT-B3LYP/6-311+G** level of theory. Both BH₂ and Co(CO)₃ fragments in these compounds are isolobal. Results indicate that -BH₂ and -Co(CO)₃ in sigmatropic shifts had similar behaviour. Furthermore, in compounds 1 and 2, prototropic shifts have similar mechanisms. In compounds 1 and 2, metallotropic shift acts faster than prototropic shift. Migration of proton and Co(CO)₃ took place through suprafacial [1,5]-sigmatropic mechanism, but -BH₂ shift took place through antarafacial [1,3]-rearrangement. The barrier energies of prototropic shift in compounds 1 and 2 are 15.94 kcal mol⁻¹ and 33.13 kcal mol⁻¹ respectively. These energies are lower than those of brotropic shifts in compound 1 (0.16 kcal mol⁻¹) or migration of CO(CO)₃ in compound 2 (3.76 kcal mol⁻¹).

Keywords: *Ab initio*, cyclopentadienyl, isolobal, metallotropic, prototropic, sigmatropy.

FLUXIONAL σ -cyclopentadienyl compounds such as (η^1 -C₅H₅)₂Hg and (η^5 -C₅H₅)(η^1 -C₅H₅)Fe(CO)₂ were first discovered by Wilkinson and Piper¹. Gridnev *et al.*² discussed the manner in which intramolecular 1,5-migrations of the metal moiety around the cyclopentadienyl ring occur. Fluxional cyclopentadienylboranes 3a-c can be prepared by transmetallation of cyclopentadienyl metals (Li, Na, Tl and Hg) at decreased temperatures (Figure 1).

Fast borotropic rearrangements in 3a-c lead to the observation of an averaged ¹H and ¹³C NMR spectra even at -105°C. The topology of borotropic migrations is unknown, the [1, 5]-B shifts have been suggested by an analogy to other metal cyclopentadienyls, but experimental evidence is insufficient. At temperatures above -10°C, 3a-c rearranges to the mixtures of vinylic boranes 3d-g and 3i-j (Figure 1). Spectroscopic studies of cyclopenta-

2,4-dienylborane such as ¹H NMR, ¹³C NMR, mass spectrometer and IR indicated that metallotropic shifts in solution state occurred much faster compared with prototropic shifts to give allylic isomers, which are nonfluxional³⁻¹⁰.

The isolobal principle in organometallic chemistry has been reported earlier¹¹. 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 far from the plane of the molecule (though they are not isoelectronic). So, it can be inferred that -BH₂ and -Co(CO)₃ are isolobal groups, whose HOMO and LUMO diagrams are shown in Figure 2.

Density functional methods (DFT) were calculated using B3LYP/6-311+G** level of theory and using the GAUSSIAN 2003 package of programs¹²⁻¹⁶. Vibrational frequency was calculated at B3LYP/6-311+G** level of theory for all ground and transition state structures. Method dependencies were studied by single-point energies computed at MP2/6-311+G** level of theory for optimized geometries. By minimizing energy regarding geometrical coordinates without imposing any symmetrical constraints, minimum energy molecular geometries were located. All transition state structures were gained by QST2 subroutine^{17,18}.

The nature of the stationary points for compounds 1 and 2 has been determined according to the number of imaginary frequencies. Only real frequency values and single imaginary frequency values (with negative sign) were accepted for minimum state and transition state structures respectively (Tables 1-3).

Results and discussion

As mentioned above, although the fluxional behaviour of boron in cyclopentadienylboranes was observed², its mechanism has not been examined. However other experimental or theoretical studies could not be accomplished regarding the structural and fluxional behaviours and sigmatropic shift mechanism of isolobal compound with cyclopentadienylboranes. *Ab initio* behaviours of

*For correspondence. (e-mail: saeed_jamehbozorgi@yahoo.com)

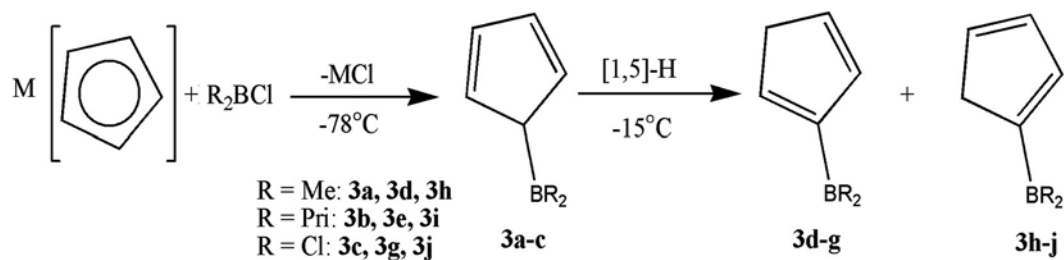


Figure 1. Preparation of cyclopentadienylboranes.

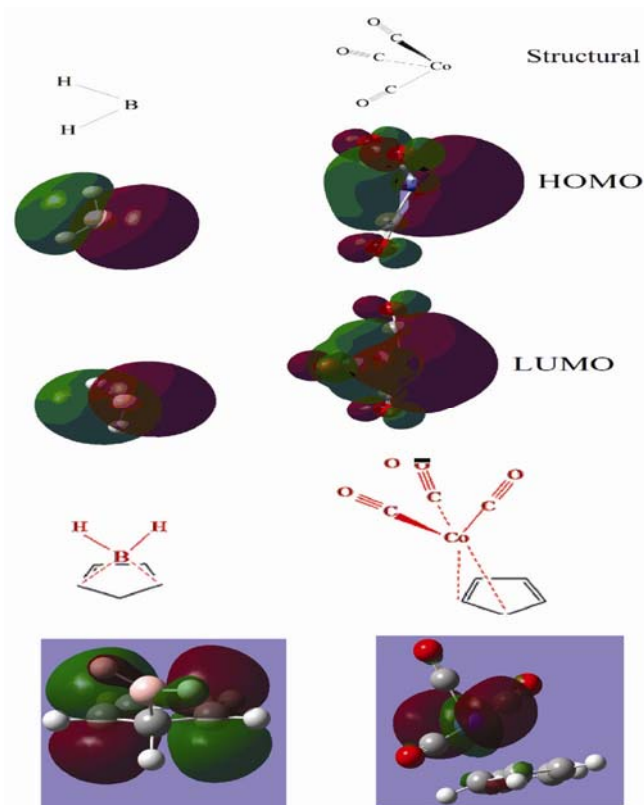


Figure 2. Optimized structural, HOMO and LUMO diagram of BH_2 and its isolobal fragment $[Co(CO)_3]$ and HOMO diagram of optimized metallotropic transition state structural of compounds **1**, **2**.

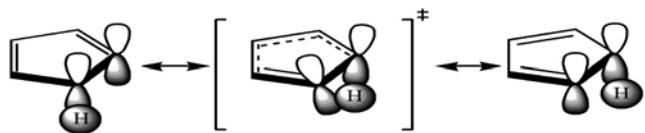


Figure 3. Symmetry-allowed suprafacial [1,5] rearrangement of proton.

metallotropic 1,2-shift and prototropic 1,2-shift of cyclopentadienyl(trimethyl)-silane, -german and -stannane were studied earlier¹⁴. Based on the present results it can be concluded that allylic isomer is the most stable isomer among the mentioned compounds. In addition, it was indicated that prototropic shift is much slower than metallotropic shift¹⁹.

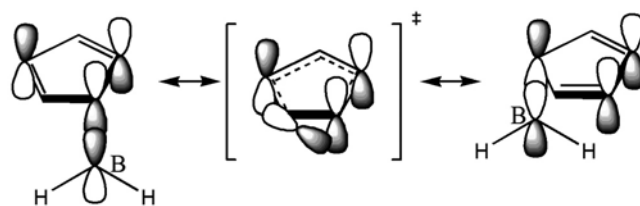


Figure 4. [1,3] Antarafacial rearrangement of BH_2 fragment.

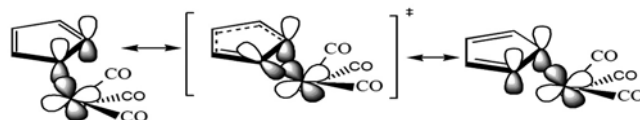


Figure 5. [1,3] Symmetry-allowed suprafacial [1,2] rearrangement of $Co(CO)_3$.

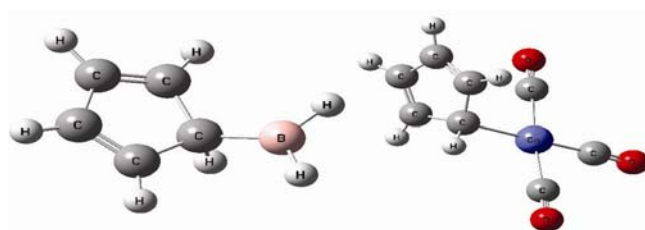


Figure 6. Structure of compounds **1** and **2**.

The 1,2-shift and hydrogen migration mechanisms for the $Co(CO)_3$ and BH_2 were studied using B3LYP/6-311+G** and MP2/6-311+G** levels of theory for compounds **1** and **2**. The main objective of this work was to study and compare the sigmatropic behaviour of cyclopenta-2,4-dienylborane (**1**), structural and fluxional characteristics and sigmatropic shift mechanism for inorganic isolobal compound with cyclopenta-2,4-dienylborane (**1**). Furthermore, mechanistic study of migration of proton, boron and isolobal groups on cyclopentadienyl ring was performed by *ab initio* molecular orbital (MO) and density functional methods (DFT), using the GAUSSIAN 2003 package programs.

In both [1, 5] hydrogen shifts were performed by a symmetry-allowed suprafacial rearrangement (Figure 3). In contrast with these, thermal [1, 5] sigmatropic hydrogen shift and thermal [1, 3] hydrogen shifts are not

Table 1. DFT-B3LYP/6-311+G** calculated structural parameters and imaginary frequency of the ground states and transition states of 1-cyclopentadienyl(dihydro)borane

Compounds	1	2	3	[1 → 2] [#]	[2 → 3] [#]	[3 → 3']	[1 → 1'] [#]
Bond lengths							
B–C	1.562	1.519	1.531	1.521	1.514	1.527	1.570
C ₁ –C ₂	1.503	1.371	1.481	1.437	1.425	1.418	1.510
C ₂ –C ₃	1.349	1.451	1.345	1.381	1.386	1.402	1.350
C ₃ –C ₄	1.464	1.354	1.505	1.417	1.422	1.500	1.463
C ₄ –C ₅	1.349	1.496	1.497	1.389	1.468	1.402	1.350
C ₅ –C ₁	1.503	1.515	1.365	1.519	1.426	1.418	1.499
C–H	1.117	1.098	1.099	1.267	1.306	1.306	1.111
Bond angles							
B–C ₁ –C ₂	119.032	125.570	128.830	129.429	128.13	126.026	80.395
C ₁ –C ₂ –C ₃	108.967	111.091	110.372	109.857	111.218	109.591	108.848
C ₂ –C ₃ –C ₄	109.343	108.634	109.187	109.591	107.914	106.437	109.444
C ₃ –C ₄ –C ₅	109.342	109.447	102.883	108.992	106.933	106.433	109.233
C ₄ –C ₅ –C ₁	108.971	104.252	110.626	107.411	107.89	109.592	109.311
Torsion angles							
B–C ₁ –C ₂ –C ₃	132.819	179.970	179.969	171.995	–179.480	179.153	–128.432
C ₁ –C ₂ –C ₃ –C ₄	1.208	0.031	–0.002	0.451	0.704	0.068	–1.552
C ₂ –C ₃ –C ₄ –C ₅	0.007	–0.023	0.003	–0.299	–0.217	0.008	0.277
C ₅ –C ₁ –C ₂ –C ₃	–1.845	–0.024	0.000	–0.407	–0.903	–0.120	2.121
Imaginary frequency	–	–	–	–1040.4292	–1128.6021	–1175.0503	–157.3694

Bond lengths are in angstrom units (Å) and angles in degrees (°).

Table 2. Calculated parameters and energies of the ground states and transition states of 1-cyclopentadienyl(dihydro)borane

Methods	1	2	3	[1 → 2] [#]	[2 → 3] [#]	[3 → 3'] [#]	[1 → 1'] [#]
DFT-B3LYP/6-311+G**//DFT-B3LYP/6-311+G**							
ZPE ^a	0.095983	0.097242	0.096919	0.0937644	0.094152	0.093751	0.09595
E _{el}	–219.5926	–219.609	–219.603	–219.565	–219.5675	–219.560	–219.5923
E ₀ = E _{el} + ZPE	–219.4966	–219.5117	–219.5060	–219.4712	–219.4733	–219.4662	–219.4963
ΔE ₀ ^b (Hartree)	0.0151	0.000	0.0057	0.0405	0.0384	0.0455	0.0153
ΔE ₀ (kcal mol ^{–1})	9.47	0.000	3.57	25.41	24.09	28.55	9.63
E _a ^c (kcal mol ^{–1})				15.94	24.09	24.98	0.16
MP2/6-311+G**//DFT-B3LYP/6-311+G**							
ZPE ^a	0.095983	0.097242	0.096919	0.0937644	0.094152	0.093751	0.095959
E _{el}	–218.8756	–218.8897	–218.8845	–218.8509	–218.8511	–218.8455	–218.8756
E ₀ = E _{el} + ZPE	–218.7797	–218.7924	–218.78758	–218.75713	–218.7569	–218.75174	–218.7796
ΔE ₀ ^b (Hartree)	0.0127	0.000	0.00482	0.0352	0.0355	0.0406	0.0128
ΔE ₀ (kcal mol ^{–1})	8.01	0.000	3.02	22.13	22.27	25.51	8.03
E _a ^c (kcal mol ^{–1})				14.29	22.27	22.49	0.02

^aCorrected by multiplying by a scaling factor (0.9409). ^bRelative to the most stable structure.

known. It is impossible for BH₂ shift to occur through [1, 5] suprafacial rearrangement. This migration is not a [1, 3] natural rearrangement (Figure 4). But Co(CO)₃ shifts can occur through [1, 5] suprafacial rearrangement (Figure 5).

The prototropic 1,5-shifts convert 5-Co(CO)₃C₅H₅ into 1-Co(CO)₃C₅H₅ and 2-Co(CO)₃C₅H₅. The hydrogen migrates stepwise from C(5) to C(1), C(1) to C(2) and then from C(2) to C(3). Unlike the Co(CO)₃ fragment migration, the rearrangements involving hydrogen migration C(5) to C(1) and C(1) to C(2) are non-degenerate and the reaction pathways are non-symmetrical (Figures 6 and

7). The prototropic shift from C(2) to C(3) has a symmetrical transition state. *Ab initio* and DFT calculations show that the energy barrier related to BH₂C₅H₅ shift of the prototropic from C(1) to C(2) is higher than that related to prototropic shift of C(2) to C(3).

HOMO diagram of transition state structure for compounds **1** and **2** is shown in Figure 2. Based on HOMO diagram of compound **1**, only one node can be observed on C(2) atom, therefore, sigmatropic shift from C(1) to C(5) is impossible, but proper overlap of frontier orbitals of BH₂ with C(1) and C(3) creates a [1, 3]-sigmatropic shift of BH₂ (Figure 2). On the other hand, HOMO

Table 3. DFT-B3LYP/6-311+G** calculated structural parameters and imaginary frequency of the ground states and transition states of 1-cyclopentadienyl(tricarbonyl)cobalt

Compounds	1	2	3	[1 → 2] [#]	[2 → 3] [#]	[3 → 3'] [#]	po
Bond lengths							
Co–C	2.083	1.934	1.970	1.966	1.930	1.984	2.204
C ₁ –C ₂	1.470	1.522	1.352	1.495	1.427	1.408	1.426
C ₂ –C ₃	1.371	1.500	1.508	1.409	1.484	1.410	1.402
C ₃ –C ₄	1.436	1.349	1.502	1.400	1.413	1.484	1.402
C ₄ –C ₅	1.394	1.459	1.347	1.398	1.392	1.410	1.426
C ₅ –C ₁	1.469	1.368	1.483	1.427	1.423	1.408	1.445
C–H	1.083	1.098	1.098	1.307	1.316	1.316	1.080
Bond angles							
Co–C ₁ –C ₂	102.870	128.991	132.153	132.389	124.088	125.551	70.85
C ₁ –C ₂ –C ₃	108.530	104.622	109.998	108.018	108.076	108.982	106.99
C ₂ –C ₃ –C ₄	108.981	108.902	103.007	108.135	106.583	106.607	108.68
C ₃ –C ₄ –C ₅	108.982	109.183	109.242	109.694	108.114	106.607	108.63
C ₄ –C ₅ –C ₁	108.531	110.892	109.790	109.612	111.52	108.98	107.00
Torsion angles							
Co–C ₁ –C ₂ –C ₃	–106.751	–167.585	180.000	–161.530	–168.819	176.949	–107.320
C ₁ –C ₂ –C ₃ –C ₄	–0.369	–0.436	–0.002	–0.092	–1.227	–0.148	–1.178
C ₂ –C ₃ –C ₄ –C ₅	0.005	–1.189	0.002	–1.550	0.344	0.000	1.930
C ₅ –C ₁ –C ₂ –C ₃	0.568	1.971	0.000	1.624	1.590	0.245	0.000
Imaginary frequency	–	–	–	–1184.3013	–1191.5635	–1227.1553	–84.0841

Bond lengths are in angstrom units (Å) and angles in degrees (°).

Table 4. Calculated energies of the ground states and transition states of 1-cyclopentadienyl-(tricarbonyl)cobalt

Methods	1	2	3	[1 → 2] [#]	[2 → 3] [#]	[3 → 3'] [#]	[1 → 1'] [#]
DFT-B3LYP/6-311+G**//DFT-B3LYP/6-311+G**							
ZPE ^a	0.10079014	0.100673	0.100167	0.096965	0.097514	0.0968722	0.100694
E _{el}	–1916.4465	–1916.4331	–1916.4328	–1916.3899	–1916.3889	–1916.3882	–1916.440
E ₀ = E _{el} + ZPE	–1916.3457	–1916.3324	–1916.3326	–1916.2929	–1916.29138	–1916.29132	–1916.33930
ΔE ₀ ^b (Hartree)	0.0000	0.0133	0.0131	0.0528	0.0543	0.05437	0.006
ΔE ₀ (kcal mol ^{–1})	0.000	8.34	8.22	33.13	34.08	34.11	3.76
ΔE _a ^c (kcal mol ^{–1})				33.13	25.74	25.89	3.76
MP2/6-311+G**//DFT-B3LYP/6-311+G**							
ZPE ^a	0.1007901	0.100673	0.100167	0.096965	0.097514	0.0968722	0.100694
E _{el}	–1913.8914	–1913.8748	–1913.8711	–1913.8322	–1913.8370	–1913.8298	–1913.8863
E ₀ = E _{el} + ZPE	–1913.7906	–1913.7741	–1913.7709	–1913.7355	–1913.7394	–1913.7329	–1913.7856
ΔE ₀ ^b (Hartree)	0.0000	0.0165	0.0197	0.0551	0.0512	0.0577	0.005
ΔE ₀ (kcal mol ^{–1})	0.000	10.35	12.36	34.57	32.12	36.20	3.13
E _a ^c (kcal mol ^{–1})				34.57	21.77	23.84	3.13

^aCorrected by multiplying by a scaling factor (0.9409). ^bRelative to the most stable structure.

diagram of compound **2** refers to the proper overlap of orbitals for [1, 5]-sigmatropic shift of Co(CO)₃ fragment, because of which no node appears on C(5) of C₅H₅ ring. Therefore, [1,5]-metallotropic shift has occurred. Reaction pathways are shown in Figures 7 and 8. The B3LYP/6-311G** calculated energies are given in Tables 1–3.

Calculated results of these compounds showed that 1,5-borotropic shift is impossible. When BH₂ is in vinylic state, these compounds can not be in ground state. Vibrational frequencies illustrate one imaginary frequency. On the other hand, when bond lengths of C–B increase to 1.57 Å, it was revealed that this structure is a transition

state (Figure 7 and Table 1). Also, according to IRC calculation in vinylic position, BH₂ is a transition structure (Figure 9). Mechanism of migration of BH₃ revealed a suprafacial [1, 5]-rearrangement (Figure 10). Results of calculating B3LYP/6-311G** level of theory showed that [1, 5] transition easily happened and the amount of required energy was 3.05 kcal mol^{–1}. Structural parameters, corrected zero point (ZPE) and total electronic (E_{el}) energies for compounds **1** and **2** calculated on the *ab initio* and DFT-B3LYP/6-311G** level are given in Tables 1–4. However, contrary to these calculated data, electron diffraction studies of the compounds Co(CO)₃C₅H₅ and

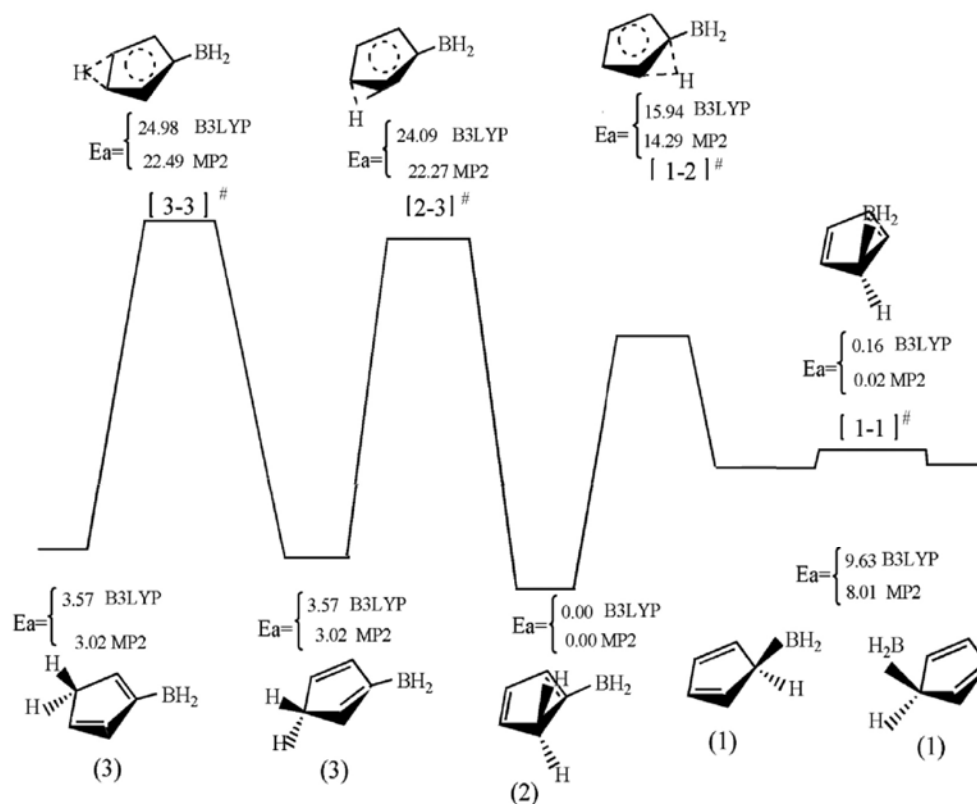


Figure 7. Calculated DFT-B3LYP/6-311+G** profile for borotropic and prototropic 1,2-shifts in cyclopentadienyl(dihydro)borane. Numbers are the corresponding E_a and E₀ values in kcal mol⁻¹.

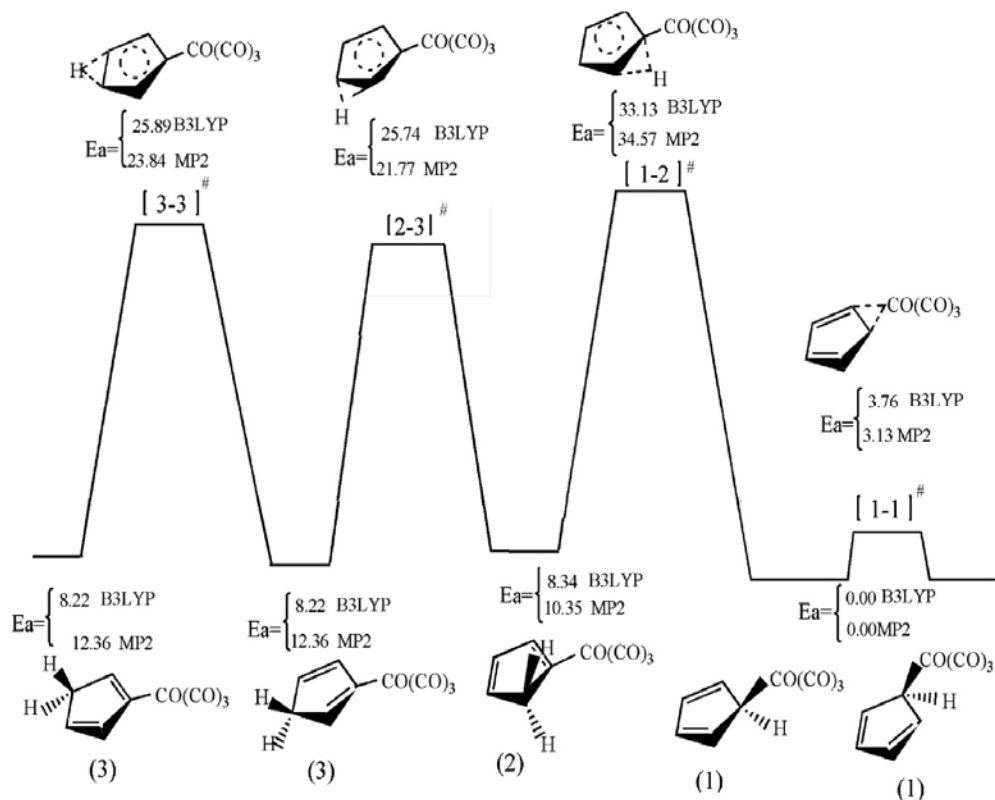


Figure 8. Calculated DFT-B3LYP/6-311+G** profile for metallotropic and prototropic 1,2-shifts in cyclopentadienyl(tricarbonyl)cobalt. Numbers are the corresponding E_a and E₀ values in kcal mol⁻¹.

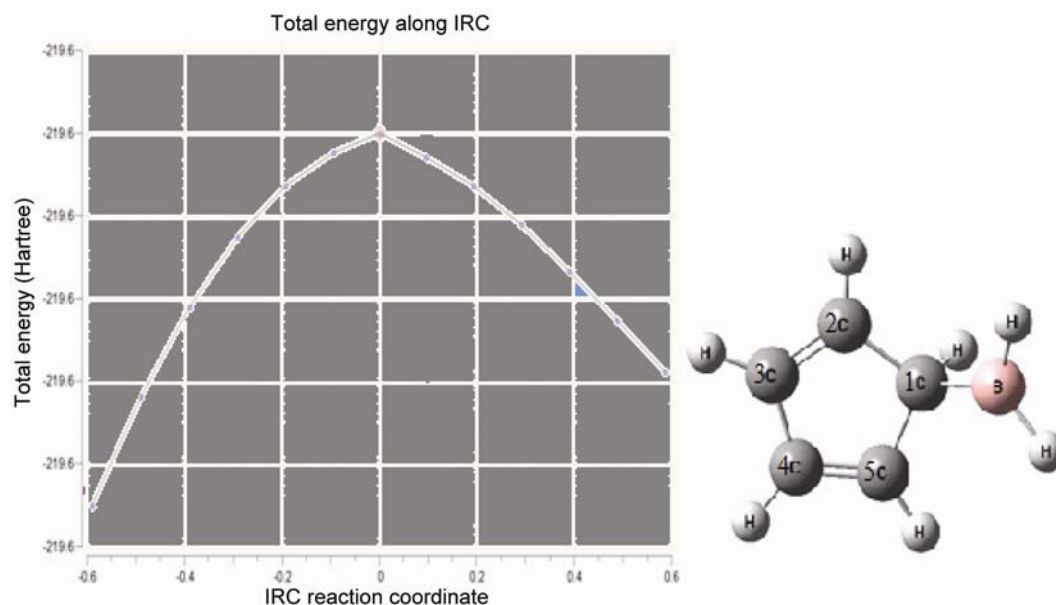


Figure 9. Calculated DFT-B3LYP/6-311+G** IRC plot of [1,5] shift for borotropic shift in cyclopentadienyl(dihydro)borane.

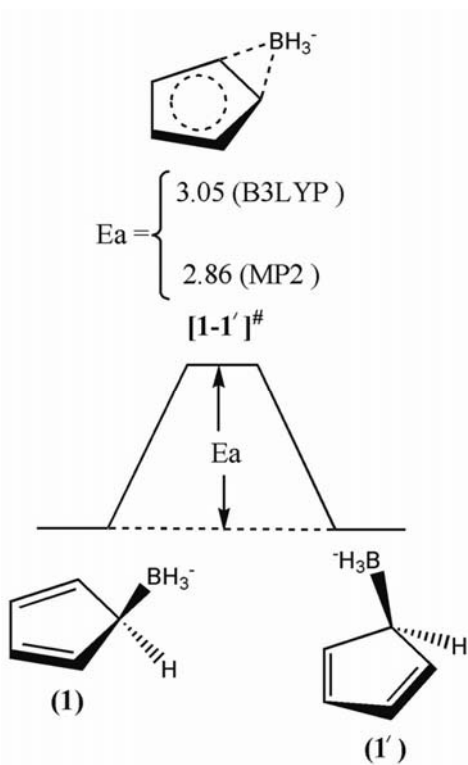


Figure 10. Calculated profile for BH_3 transition. Numbers are the corresponding E_a values in kcal mol^{-1} .

$(\text{BH}_2)\text{C}_5\text{H}_5$ have shown that the C_5H_5 rings are essentially planar^{16,17}. Studies on the DFT/6-311G** level of theory indicate a planar C_5H_5 ring in the ground state structure of compounds **1** and **2**. The 1,5-shift mechanisms of BH_2 , $\text{Co}(\text{CO})_3$ and hydrogen migrations are examined.

Furthermore, reaction pathways are shown in Figures 7 and 8. In metallotropic 1,5-shifts, the pathways reaction are symmetrical and in the transition state structure, the BH_2 , $\text{Co}(\text{CO})_3$ groups are equidistant from two carbon atoms of the C_5H_5 ring (Tables 1 and 3). These results indicate that when compared to C–B, the lengths of C–Co bond increase, but in contrast the dissociation of a C–B bond is easier than that of a C–Co bond which in turn, cause migration of the metal around the cyclopentadienyl ring with a lower energy barrier. This result is consistent with experimental data.

As can be inferred from Figures 7 and 8, the prototropic 1,5-shifts compared to metallotropic 1,5-shifts, are much slower than those of metal migration. It can be concluded that the prototropic 1,5-shifts occur only at higher temperatures. This reaction mechanism was carried out for BH_2 migration, which revealed that BH_2 [1, 5] migration needs $0.16 \text{ kcal mol}^{-1}$, which is a lower migration energy than $\text{Co}(\text{CO})_3$ (3 kcal mol^{-1}). However, bond lengths of C–B and C–Co are 1.562 and 2.095 \AA respectively. The reason for the higher level of barrier energy for $\text{Co}(\text{CO})_3$ is probably related to the existence of a π back bonding between Co and C. Also, it is clear that prototropic shifts for compound **1** have migration energy lower than those for compound **2**.

Conclusions

The results were calculated by B3LYP/6-311+G** and MP2/6-311+G** and it refers to the fact that allylic isomers are the most stable isomers of compounds **1** and **2**. Bond length of B–C is longer than Co–C. However, sigmatropic barrier energy for BH_2 migration is higher than

that of $\text{Co}(\text{CO})_3$, because of a π -back bonding in $\text{Co}-\text{C}$ bond which makes it stronger than $\text{B}-\text{C}$. Finally, instead of 1,5- BH_2 shift, kind of [1, 3] shift occurs for borotropic, while for its isolobal fragment $\text{Co}(\text{CO})_3$ [1, 5] transition was easier. Similarity, the occurrence of [1, 5]-prototropic shift for both compounds was simple. Prototropic shift activation energy is lower than borotropic shift. It is also worth pointing out that, lower amount of activation energy in borotropic shift can result in the rotation of boron on the cyclopentadienyl ring in the ambient temperature.

Results of structural calculations and IR studies showed that prototropic and metallotropic shifts are [1, 5]-sigmatropic migrations but borotropic shift is similar to metallotropic shift [1, 3].

1. Wilkinson, G. and Piper, T. S., Cyclopentadienyl-triethylphosphine-copper(I) and bis-cyclopentadienylmercury(II). *Inorg. Nucl. Chem.*, 1956, **2**, 32–37; Piper, T. S. and Wilkinson, G., Piper, T. S. and Wilkinson, G., Alkyl and aryl derivatives of Π -cyclopentadienyl compounds of chromium, molybdenum, tungsten, and iron. *Inorg. Nucl. Chem.*, 1956, **3**, 104–124.
2. Gridnev, I. D., Gurskii, M. E., Ignatenko, A. V., Bubnov, Yu. N. and Il'ichev, Y. V., A series of sigmatropic rearrangements in 2,4,6-heptatrienyl(dipropyl)-borane. Kinetic study of [1,7] hydrogen shift facilitated by [1,3] boron shifts. *Organometal. A Organometal.*, 1993, **12**, 2487–2495.
3. Kisin, A. V., Kovenevsky, V. A., Sergeyev, N. M., Ustynyuk, Yu. A., Nuclear magnetic resonance spectroscopy of metal cyclopentadienyls VI. Metallotropic rearrangement in the group IVB cyclopentadienyls. *J. Organomet. Chem.*, 1972, **34**, 93–104.
4. Ustynyuk, Y. A., Zakharov, P. I., Azizov, A. A., Potapov, V. K. and Pribytkova, I. M., Mass spectra of monohapto-cyclopentadienyl derivatives of group IVB elements., *J. Organomet. Chem.* 1975, **88**, 37–64.
5. Grishin, Y. K., Sergeyev, N. M. and Ustynyuk, Yu. A., ^{13}C NMR spectra of metal σ -cyclopentadienyls. *J. Organomet. Magn. Reson.*, 1972, **4**, 377–390.
6. Hagen, A. P. and Russa, P. J., Fluxional behavior of 5-(silyl)cyclopentadiene and 5-(silyl)methylcyclopentadiene (1,2-isomer mixture). *J. Organomet. Chem.*, 1973, **51**, 125–133.
7. Davison, A. and Rakita, P. E., Fluxional behavior of cyclopentadienyl, methylcyclopentadienyl, and pentamethylcyclopentadienyl compounds of silicon, germanium, and tin. *Inorg. Chem.*, 1970, **9**, 289–294.
8. Angus, P. C. and Stobart, S. R., Stereochemical non-rigidity in germylcyclopentadiene and related derivatives of germane. *J. Chem. Soc. Dalton. Trans.*, 1973, 2374–2380.
9. Sergeyev, N. M., Avramenko, G. I., Kisin, A. V., Kovenevsky, V. A. and Ustynyuk, Y. A., Nuclear magnetic resonance spectroscopy of metal cyclopentadienyls V. Metallotropic rearrangement in silicon cyclopentadienyls: 1,2 shift and spectral regularities in σ -cyclopentadienyls. *J. Organomet. Chem.*, 1971, **32**, 55–77.
10. Cuthbertson, A. F. and Glidewell, C., The structure of silyl cyclopentadienes. *J. Organomet. Chem.*, 1981, **221**, 19–31.
11. Hoffmann, R., Building bridges between inorganic and organic chemistry. *Ange. Chem. Int. Ed.* 1982, **21**, 711–724.
12. Becke, A. D., Perspective on density functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.*, 1993, **98**, 5648–5652.
13. Lee, C., Yang, W. and Parr, R. G., Development of the Colle–Salvetti correlation–energy formula into a functional of the electron density. *Phys. Rev.*, 1998, **37**, 785–789.
14. Hehre, W. J., Radom, L., Schleyer, P. V. R. and Pople, J. A., *Ab initio Molecular Orbital Theory*, Wiley, New York, 1986.
15. Seminario, J. M. and Politzer, P. (eds), *Modern Density Function Theory, A Tool for Chemistry*, Elsevier, Amsterdam, 1995.
16. Frisch, M. J. *et al.*, GAUSSIAN 98 (Revision A3) Gaussian Inc, Pittsburgh PA, 1998.
17. Peng, C. and Schlegel, H. B., Combining synchronous transit and quasi-Newton methods to find transition states. *Israel J. Chem.*, 1993, **33**, 449–454.
18. Peng, C., Ayala, P. Y., Schlegel, H. B. and Frisch, M. J., Using redundant internal coordinates to optimize equilibrium geometries and transition states. *J. Comp. Chem.*, 1996, **17**, 49–56.
19. Nori-Shargh, D., Aghabozorgh, H., Zare, K., Talei, M. R. and Jameh-Bozorgh, S., *Ab initio* study of structures, metallotropic 1,2-shifts and prototropic 1,2-shifts of cyclopentadienyl(trimethyl)silane, -germane and -stannane. *Phosphorus Sulfur Silicon*, 2003, **178**, 341–351.

Received 20 April 2016; revised accepted 25 July 2016

doi: 10.18520/cs/v112/i04/743-749