Density Functional Study of Molecular Orbitals of Cobaltocene and Nickelocene Molecules

Abstract
The electronic structure and geometry optimization of cobaltocene and nickelocene molecules are calculated using DFT/B3LYP with the basis set of 6-31G (d). The Eigen values, Eigen vector and population analysis of the molecules show that the first 12 molecular orbitals in cobaltocene and 14 in nickelocene have contribution from 2pz orbitals of carbon of (C5H5)- and 4s, 4p and 3d orbitals of cobalt and nickel respectively. We found that the extent of involvement of metal orbitals in the two cases is different. In cobaltocene the maximum involvement out of 4s and 4p orbital is in the order 4s>4pz>4py>4px and in 3d orbitals the order is 3dyz>3dxz>3dz2>3dxy>3dyx>3d2z>3dx2-y2. The involvement of corresponding orbital in nickelocene with respect to the 4s and 4p orbitals is in the order of 4py>4px>4s>4pz and in 3d orbitals the order is 3dyz>3dx2-y2>3dxy>3dxz>3dz2 molecules. The total involvement of 3d, 4s and 4p orbitals of metal and 2pz orbitals of the ten carbon atoms of both ligands of (C5H5)- in cobaltocene and nickelocene respectively are 40.2388 and 38.3776 hence we can conclude that cobaltocene is more stable than nickelocene. Similar results are found from calculation of parameters like dipole moment, HOMO-LUMO gap and Mullikan charge distribution. The population analysis shows that only 2pz orbitals of carbon of (C5H5)- and 3d orbitals of metal provide electrons to MOs of cobaltocene and nickelocene.

Keywords: Cobaltocene; Nickelocene; Eigen vector; Population analysis; Eigen values; Atomic and molecular orbitals

Introduction
In the last decade, there has been a phenomenal advancement in theoretical inorganic chemistry [1,2], much faster computers are available and commercial programs incorporating the latest methods have become widely available and are capable of providing more information about molecular orbitals (MOs), with a sample input of chemical formula. The focus of attention has been on computational transition-metal chemistry [3,4]. This is largely due to the successful employment of gradient corrected density functional theory in calculating molecules, particularly of the heavier atoms [5-8] and in the use of small-core relativistic effective core potential [9-11] which set the stage for calculation of geometries, bond energies, and chemical reaction and other important properties of transition metal compounds with impressive accuracy [8,12]. Application of density functional calculation to organometallic [13,14] and transition metal compounds is growing [15] density functional parameters such as eigenvectors, eigenvalues and population analysis are well calculated with this method. In this paper present the calculations of Eigen vectors, Eigen values and population analysis of cobaltocene and nickelocene in order to study the extent of contribution of 3d, 4s and 4p orbital in the formation of MOs. Such a quantitative study will provide correct information about the involvement of 4p orbital of cobalt and nickel in bonding will help to resolve the controversy raised by other workers [16-20].

Materials and Methods
In computational chemistry tools the DFT offers the fundamentals for interpreting multiple chemical concepts used in different branches of chemistry. In modern computational chemistry, quantum chemical calculations are typically performed with in a finite set of basic functions. When molecular calculations are
performed, it is common to use a basis sets composed of a finite number of atomic orbitals, centered at each atomic nucleus with in the molecule, for example linear combination of atomic orbitals. The methods most commonly used for this research are DFT/B3LYP

1. combination of Beck’s three-parameter exchange functional and Lee-Yang-Parr correlation functional with 6-31G
2. basis set.

These methods are found in Gaussian 03W program. B3LYP is a DFT method with hybrid functional that provides qualitative accuracy [21]. By using these methods we have optimized the energy, Eigen values, Eigen vector, population analysis, HOMO-LUMO energy gap, hardness, softness, electronegativity, visualize the HOMO and LUMO orbitals’ of cobaltocene and nickelocene molecules. The coefficients in linear combination for each molecular orbital being found by solution of the Roothaan-equation. A widely used method to analyze SCF wave function is population analysis, introduced by Mullikan population methods [22].

Results and Discussion

This research is aimed to study the electronic structure and optimized geometry of cobaltocene and nickelocene molecules. Geometry optimization is used to find minima on the potential energy surface representing equilibrium structure and used to obtain structure for a single-point quantum mechanical calculation, which provides a large set of structural and electronic properties. The electronic structure and geometry of cobaltocene and nickelocene molecules are found through DFT/B3LYP with a basis set of 6-31G (d) calculations. The optimized structures of these two compounds are shown in Figure 1A and 1B respectively for cobaltocene and nickelocene. The significant computed parameters are available in Tables 1 and 2 including the bond lengths, bond angles and dihedral angles of these two compounds. The optimized bond length of C-C double and single bonds in cobaltocene rings fall 1.36-1.96˚A, and nickelocene 1.392-1.98˚A at DFT/B3LYP, levels through 6-31G (d) basis set. There are two types of C-C bonds involved in these species. These are C-C single bonds and C-C double bonds of cobaltocene and nickelocene and according to its bond length are in the order of C=C-C-C. From Tables 1 and 2 we observed slight difference in the bond lengths, bond angles and dihedral angles throughout the molecules of ferrocene and nickelocene. This indicates that the aromatic cobalt atom in cobaltocene and nickel atom in nickelocene are relatively stable metabolically. As shown in Figure 2A and Table 1 the bond connectivity of Co-(C₅H₅)₂ of the two ligands are asymmetrical. The optimized bond length of cobalt atom with the two carbon atoms has fewer variations. The cobalt atom in cobaltocene is bonded with C2 atom of bond length 1.969 (˚A) in one side of the ligand and with C12 of bond length 1.994 (˚A) on the opposite side. In the cobaltocene molecule the cobalt atom is located between the two ligands but inclined by -80.623 measured from the plane of the cyclopentadienyl and the two ligands are parallel but with a slide of one from the other by a center of mass separation 1.33˚A. As shown in Figure 2B and Table 2. The bond connectivity of Ni-(C₅H₅)₂ of the two ligands are asymmetrical. The nickel atom in nickelocene is bonded with C12 atom of bond length 1.976 (˚A) only from one side of the ligand. This is due to the weak ligand fields of nickelocene having high spin arrangement with two d electrons and low spin arrangement with six d electrons of nickel atom which resulted in more reactivity of nickelocene molecule with respect to the other two molecules. In the nickelocene molecule the nickel atom is located between the two ligands but inclined by -67.377o as measured from the plane of the cyclopentadiene and the two ligands are almost parallel but with a slide of one from the other by a center of mass separation of only 0.22˚A. Generally comparing the bond length and bond angles between metal atom and carbon in cobaltocene and nickelocene molecules the former molecule possesses higher bond angles and the later molecule possesses larger bond length. The large the bond length the less stability but more reactivity, hence nickelocene is more reactive and less stable than the cobaltocene. In the calculations of Mullikan charge distributions of cobaltocene and nickelocene molecules, given in Figure 3. The red color indicates for excess of negative charges (-ve) while the green color indicates for excess of positive charges (+ve) among the bonded atoms, where electrons can flow from positions of excess of negative charges (-ve) to the positions of excess of positive charges (+ve). Energies of molecular orbitals are called Eigen values. The main focus has been on the molecular structure
and the properties that will be evaluated can be used to determine the molecular reactivity as well as the molecular stability. The HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are very important aspects to consider for these types of observations. This is because the HOMO and LUMO are the most likely locations where reaction will occur. The reaction is likely to occur there because the electrons in the HOMO have the highest energy and therefore the electrons are most willing to react. The LUMO is likely the location for a bond to occur as well because any invading electrons for another molecule will fill in to the LUMO, that is why comparing the energies of these orbitals create an idea of how reactive a molecule is important parametric properties of the molecules at the DFT/B3LYP levels in 6-31G (d) basis set has been calculated and are given in Table 3. At the DFT/B3LYP level the HOMO energy of cobaltocene is -0.6452 eV which is slightly more negative than nickelocene of -0.6427 eV and the LUMO energy of cobaltocene is -0.5626 eV, and nickelocene -0.5614 eV. The HOMO-LUMO gap of cobaltocene and nickelocene are 0.0826 and 0.0813 eV respectively. These proves that the positions of HOMO, LUMO and the HOMO-LUMO gap can predict the stability and reactivity of the molecules, and the cobaltocene molecule shows relatively high energy gap value and the data here suggested that cobaltocene is relatively less reactive and more stable than nickelocene molecule. The most stable MO energy of cobaltocene and nickelocene are respectively -277.5151 -eV, and -295.6703 -eV. In general the HOMO and LUMO energy gap reveals the chemical activity of the molecules. LUMO as an electron acceptor represents the ability to obtain an electron (i.e. the electron affinity) and HOMO as an electron donor represents the ability to donate an electron from its orbital (i.e. the Ionization Potential). The less values in the HOMO-LUMO energy gap explains eventually charge transfer interaction taking place within the molecules. Hard molecules have large HOMO-LUMO energy gaps and soft molecule have small HOMO-LUMO energy gaps. So soft molecules (molecules with small energy gap) are favorable for easy reaction. This description also supports for cobaltocene and nickelocene molecule, cobaltocene is harder than nickelocene. In Table 3 the HOMO-LUMO gap, as a characteristic

| Entry | Bond length(Å) | Entry | Bond angle (°) | Entry | Bond angle (°) | Dihedral angle (°) |
|-------|---------------|-------|---------------|-------|---------------|-------------------|
| C1-C2 | 1.424         | C1-C2-C4 | 106.85        | C6-C1-C2-C4 | -174.834       |
| C2-C4 | 1.419         | C2-C1-C6 | 108.85        | C2-C1-C6-C8  | -8.963         |
| C1-C6 | 1.448         | C1-C6-C8  | 107.56        | C1-C2-C4-C8  | 6.05           |
| C6-C8 | 1.391         | C10-C11-C14 | 93.45       | C10-C11-C14-C16 | -85.112    |
| C10-C11 | 1.471         | C12-C10-C11 | 97.468     | C12-C10-C11-C14 | 87.862    |
| C10-C12 | 1.427         | C10-C12-C16 | 105.11     | C10-C11-C14-C16 | 82.95     |
| C11-C14 | 1.366         | Ni-C12-C10 | 72.433      | C14-C16-C12-Ni | -67.377    |
| C12-C16 | 1.427         | Ni-C2-Ni  |               |               |               |

**Table 1** The selected bond lengths in Å, some bond angles and dihedral angles of the optimized structure of cobaltocene using DFT levels with B3LYP/6-31G (d) basis set.

| Entry | Bond length(Å) | Entry | Bond angle (°) | Entry | Bond angle (°) | Dihedral angle (°) |
|-------|---------------|-------|---------------|-------|---------------|-------------------|
| C1-C2 | 1.509         | C6-C1-C2 | 109.511       | C6-C1-C2-C4 | 0.027          |
| C1-C6 | 1.509         | C8-C6-C1 | 109.511       | C8-C6-C1-C4 | -0.028        |
| C8-C6 | 1.359         | C10-C11-C1 | 109.511     | C10-C11-C14-C16 | -78.168   |
| C10-C11 | 1.509         | C10-C12-C1 | 109.56      | C16-C12-C10-C11 | 84.623    |
| C10-C12 | 1.509         | Co-C2-C1 | 79.123       | Co-C2-C1-C6  | -80.623       |
| C11-C14 | 1.909         |       |               |               |               |
| C12-C16 | 1.559         |       |               |               |               |
| C2-C4 | 1.359         |       |               |               |               |
| C4-C8 | 1.87          |       |               |               |               |

**Table 2** The selected bond length Å, bond angles and dihedral angles of the optimized structure of nickelocene using DFT levels with B3LYP/6-31G (d) basis set.

| Molecular properties | cobaltocene | nickelocene |
|---------------------|-------------|-------------|
| RB-HF-LYP (eV)      | -1769.5679  | -1650.74    |
| εHOMO(eV)           | -0.6452     | -0.6427     |
| εLUMO(eV)           | -0.5626     | -0.5614     |
| εLUMO+εHOMOenergy gap (eV) | 0.0826 | 0.0813 |
| Ionization potential(I in eV) | 0.6452 | 0.6427 |
| Electron affinity(A in eV) | 0.5626 | 0.5614 |
| Global hardness (\(\eta\) in eV) | 0.04129 | 0.04065 |
| Global softness (\(S\) in eV) | 24.216 | 24.603 |
| Electro negativity (\(\chi\) in eV) | 0.6039 | 0.6021 |
| Chemical potential (\(\mu\) in eV) | -0.6039 | -0.6021 |
| Dipole moment (\(\mu\) in Debye) | 1.695 | 1.931 |
| Mulliken charge distributions (M.C.D in e) | ± 1.13 | ± 1.692 |

**Table 3** Important parametric properties of the molecules calculated at the DFT/B3LYP Levels in 6-31G (d) basis set.
of reactivity, shows cobaltocene has lower chemical reactivity comparing to nickelocene molecule. Absolute hardness and softness are important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap. So for more energetically stable and less reactive cobaltocene molecule, the HOMO-LUMO energy gap and hardness, \( \eta \) is larger comparing to nickelocene molecules. The dipole moments and Mulliken charge ranges as displayed in Table 3. Nickelocene would have more charge than the cobaltocene molecule. This is due to higher dipole moment and lower HOMO-LUMO energy gap indicated that the molecule is better reactive. This indicates that nickelocenies more polar so that it will react with polar solvents like water. Since the separation between mass centers of the two ligands is small. The higher the dipole moment, the more polar a molecule is. This could mean that the receptor is more likely to accept polar molecules into its active site. The receptor’s active sites may serve as home to atoms that have very high electron affinities that attract the negatively charged end of a polar molecule. The above figures shows the visualized structures of cobaltocene and nickelocene show the population of electrons on their orbitals. The HOMO Orbitals represented by green color, whereas for LUMO, it is represented by red color. The red color represents the negatively charged areas of surface (i.e. those areas where accepting the electrophiles is most favorable) while the green color represents the positively charged areas of surface (i.e. those areas where accepting the nucleophiles is more favorable). The electron density of HOMO and LUMO of cobaltocene and nickelocene molecule are concentrated throughout the compound except at the right and left terminals where some of the \( \pi^* \) orbitals may be empty. Eigen vector values of atomic orbitals have been evaluated for the study of linear combination of atomic orbitals (LCAO). The MOs of cobaltocene and nickelocene are formed by linear combination of fifty AO\s of two \((C_5H_5)^-\) and nine orbital of cobalt and nickel. These fifty-nine AO\s \( \chi_1 \) to \( \chi_{59} \) on LCAO approximation form same number of MO\s, \( \Phi_1 \) to \( \Phi_{59} \). The AOs \( \chi_1 \) to \( \chi_{40} \) for 2s, 2px, 2py, 2pz of 1C to 10C, \( \chi_{41} \) to \( \chi_{49} \) for 4s, 4px, 4py, 4pz, 3dxz, 3dxy, 3dz, 3dyz of 11M and \( \chi_{50} \) to \( \chi_{59} \) for 1s of 12H to 21H respectively, where M=Co and Ni, for cobaltocene and nickelocene, respectively. The 2s, 2px and 2py orbitals of each carbon atom of \((C_5H_5)^-\) are comparatively free for complex formation is given below:

### Table 3

| Electron Configuration | Atomic Orbital       |
|-----------------------|----------------------|
| 2s                    | \( 2s \)              |
| 2px                   | \( 2px \)             |
| 2py                   | \( 2py \)             |
| 2pz                   | \( 2pz \)             |
| 3s                     | \( 3s \)              |
| 3px                   | \( 3px \)             |
| 3py                   | \( 3py \)             |
| 3pz                   | \( 3pz \)             |
| 4s                     | \( 4s \)              |
| 4px                   | \( 4px \)             |
| 4py                   | \( 4py \)             |
| 4pz                   | \( 4pz \)             |
| 5s                     | \( 5s \)              |
| 5px                   | \( 5px \)             |
| 5py                   | \( 5py \)             |
| 5pz                   | \( 5pz \)             |

The summation values shown in Table 5 and plotted in Figure 5 show the total contributions from each atomic orbital. It is clearly indicated that 4s orbital has the maximum involvement out of 4s and 4p orbital and 3dyz orbital has the maximum involvement out of 3d orbitals. The sequence from the two series is given below:

### Table 5

| Atomic Orbital | Contribution |
|---------------|--------------|
| 4s            | 4p>4p>4p>4p>
| 4px          | 4py>4py>4py>
| 4py          | 4pz>4pz>4pz>
| 4pz          | 4s>4s>4s>4s>
| 5s            | 5p>5p>5p>5p>
| 5px          | 5py>5py>5py>
| 5py          | 5pz>5pz>5pz>

The sum of contributions of atomic orbitals of cobalt in the formation of molecular orbitals of cobaltocene is shown in Table 5 and Figure 5. That the sum of contributions of 3dx\(^2\)-y\(^2\) orbital in the formation of molecular orbitals is least out of the 3d orbitals and 4px orbital is least out of 4s and 4p orbitals. Hence 3dx\(^2\)-y\(^2\) and 4px are comparatively free for complex formations. The exact order of availability of atomic orbitals of Co in cobaltocene for complex formation is given below:

### Table 6

| Atomic Orbital | Contribution |
|---------------|--------------|
| 4px          | 4py>4py>4p>
| 4py          | 4pz>4pz>4pz>
| 4pz          | 4s>4s>4s>4s>

The summation values shown in Table 7 and Figure 6, clearly indicates that contribution of 2pz orbital of \((C_5H_5)^-\) has the maximum involvement out of the ten carbon atoms in \((C_5H_5)^-\). The sequence from the series is given below:

### Table 7

| Atomic Orbital | Contribution |
|---------------|--------------|
| 6C            | 8C>10C>12C>
| 8C            | 6C>8C>10C>12C>
| 10C           | 6C>8C>10C>12C>

Sum of contributions of atomic orbitals of carbon (2pz) in the formation of molecular orbitals of cobaltocene is shown in Table 7 and Figure 6 where the sum of contribution of 14\( _{c} \) of 2pz orbital's in the formation of molecular orbital's are least out of the ten carbon atoms. Hence 14\( _{c} \) are comparatively free for
Table 4 Contributions of orbitals of cobalt and their summation values in the formation of molecular orbitals of cobaltocene.

| MOs | 4s     | 4px    | 4py    | 4pz    | 3dx²-y² | 3dz²   | 3dxy   | 3dxz   | 3dyz   |
|-----|--------|--------|--------|--------|---------|--------|--------|--------|--------|
|     | χ41    | χ42    | χ43    | χ44    | χ45     | χ46    | χ47    | χ48    | χ49    |
| 020 | -       | -      | -      | -      | -       | -      | -      | -      | -      |
| 021 | -       | -      | -      | -      | -       | -      | -      | -      | 0.2113 |
| 022 | -       | -      | -      | -      | -       | -      | -      | 0.2507 | 0.4737 |
| 023 | -       | -      | -      | 0.5537 | 0.1378  | 0.4186 | 0.1448 | 0.2731 |
| 024 | 0.1198  | -      | -      | -      | -       | -      | -      | 0.5281 | -      |
| 025 | -       | -      | -      | 0.2652 | 0.1081  | 0.5281 | 0.3717 | 0.3033 | 0.5717 |
| 026 | -       | -      | -      | 0.1445 | -       | -      | -      | 0.2391 | 0.2063 |
| 027 | -       | -      | -      | 0.1103 | 0.1402  | 0.2339 | -      | 0.2297 |
| 028 | -       | -      | -      | -      | -       | -      | -      | 0.2052 | 0.2116 |
| 029 | -       | -      | -      | -      | 0.5131  | 0.2416 | 0.3996 | 0.1363 |
| 030 | -       | -      | -      | -      | 0.3741  | -      | -      | 0.3523 | 0.4225 |
| 031 | -       | -      | -      | -      | -       | -      | -      | -      | -      |
| 032 | 0.3346  | 0.9288 | -      | 0.407  | -       | -      | -      | -      | -      |
| 033 | 0.3259  | -      | 0.8777 | 0.565  | -       | -      | -      | -      | -      |
| 034 | 0.6188  | -      | -      | 0.2691 | -       | -      | -      | -      | -      |
| 035 | 0.3195  | -      | 0.3626 | 0.4823 | -       | -      | -      | -      | -      |
| 036 | 0.3148  | -      | 0.3549 | 0.3479 | -       | -      | -      | -      | -      |
| 037 | 0.2767  | 0.3026 | -      | 0.3002 | -       | -      | -      | -      | -      |
| 038 | 0.3329  | -      | 0.2698 | 0.2911 | -       | -      | -      | -      | -      |
| 039 | 0.7259  | -      | 0.2913 | 0.3794 | -       | -      | -      | -      | -      |
| 040 | 0.5741  | 0.5317 | 0.3413 | 0.7871 | -       | -      | -      | -      | -      |
| 041 | -       | 0.238  | 0.2945 | 0.2227 | -       | -      | -      | -      | -      |
| 042 | 0.3738  | 0.2889 | 0.3878 | -      | -       | -      | -      | -      | -      |
| 043 | 0.2297  | -      | -      | 2.3685 | -       | -      | -      | -      | -      |

N.B: orbitals having coefficient values above 0.10 have only been considered.

Table 5 Sum of contributions and reactivity of atomic orbital's of cobalt in the formation of molecular orbitals of cobaltocene.

| Atomic orbital’s of Co | Sum of contributions of orbital’s of Co | Sum of reactivity |
|------------------------|-----------------------------------------|------------------|
| 4s                     | 4.5465                                  | 0.2199           |
| 4p_x                   | 2.29                                    | 0.4367           |
| 4p_y                   | 3.1799                                  | 0.3145           |
| 4p_z                   | 4.0518                                  | 0.2468           |
| 3dx²-y²                | 1.6985                                  | 0.58875          |
| 3d_x                   | 2.1062                                  | 0.4748           |
| 3d_y                   | 2.4046                                  | 0.4159           |
| 3d_z                   | 2.3685                                  | 0.4222           |
| 3d_zy                  | 2.6152                                  | 0.3824           |

Figure 4 The left side of HOMO and the right side of LUMO surfaces of cobaltocene and nickelocene molecules down of the column respectively.

Figure 5 Sum of contributions and reactivity of atomic orbital’s of Co in the formation of molecular orbitals of cobaltocene.

Figure 6 Sum of contributions and reactivity of atomic orbital’s of, carbon in the formation of molecular orbitals of cobaltocene.

complex formations. The exact order of availability of carbon atom for complex formation is given below:
Out of 59 molecular orbital Eigen values of nickelocene we shall discuss only 25 of them described in Table 8, for nickel orbitals and Table 10, for carbon orbitals. The first 14 MOs are Φ15-Φ16, Φ18-Φ20, Φ21 and Φ23-Φ30, are formed by various 3d and 2pz orbitals of (C\(_5\)H\(_5\))\(^-\). These orbitals with energies in the range of -9.9338 to -0.64271eV are the most stable molecular orbital between nickel and 2pz orbital of (C\(_5\)H\(_5\))\(^-\). The next eleven MOs i.e. Φ36-Φ40, Φ42-Φ43, Φ50, Φ53, Φ54 and Φ59 are formed by interaction of 4s, 4px, 4py and 4pz orbital of metal and 2pz orbital of carbon of (C\(_5\)H\(_5\))\(^-\). These MOs with energies in the range -0.56142 to -0.10622 eV are comparatively less stable. To examine the extent of involvement of 3d, 4s, 4p and 2pz orbitals in the formation of molecular orbitals the values of coefficient of each orbital are tabulated in Table 8.

The summation values given in Table 9 and plotted in Figure 7 show the total contributions from each atomic orbital. It is clearly indicated that 4py orbital has the maximum involvement out of 4s and 4p orbital and 3dyz orbital has the maximum involvement out of 3d orbitals. The sequence from the two series is given below:

4py > 4px > 4s > 4pz and 3dyz > 3dx\(^2\)-\(y^2\) > 3dxy > 3dxz > 3d\(^2\)z

Sum of contributions of atomic orbitals of nickel in the formation of molecular orbitals of cobaltocene is shown in Table 9 and Figure 7 that the sum of contributions of 3d\(^2\)z orbital in the formation of molecular orbitals is least out of the 3d orbitals and 4pz orbital is least out of 4s and 4p orbitals. Hence 3d\(^2\)z and 4pz are comparatively free for complex formations. The exact order of availability of atomic orbitals of Ni in nickelocene for complex formation is given below:

4pz > 4s > 4px and 3dyz > 3dxy > 3dxz > 3d\(^2\)z

The summation values shown in Table 11 and Figure 8 clearly indicates that contribution of 2pz orbital of C has the maximum involvement out of the ten carbon atoms in (C\(_5\)H\(_5\))\(^-\). The sequence from the series are given below:

4pz > 4s > 4px > 4py and 3dyz > 3dxz > 3dxy > 3dx-y^2 > 3dyz

Table 6 Contributions of 2pz orbitals of carbon atoms in (C\(_5\)H\(_5\))\(^-\) in the formation of molecular orbitals of cobaltocene.

| MOs   | 1C  | 2C  | 4C  | 6C  | 8C  | 10C | 11C | 12C | 14C | 16C |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| \(\chi^4\) | 0.3731 | - | - | - | - | - | - | - | - | - |
| \(\chi^8\) | - | - | - | - | - | - | - | - | - | - |
| \(\chi^{12}\) | - | - | - | - | - | - | - | - | - | - |
| \(\chi^{16}\) | - | - | - | - | - | - | - | - | - | - |
| \(\chi^{20}\) | - | - | - | - | - | - | - | - | - | - |
| \(\chi^{24}\) | 0.3214 | - | - | - | - | - | - | - | - | - |
| \(\chi^{28}\) | - | - | - | - | - | - | - | - | - | - |
| \(\chi^{32}\) | - | - | - | - | - | - | - | - | - | - |
| \(\chi^{36}\) | - | - | - | - | - | - | - | - | - | - |
| \(\chi^{40}\) | - | - | - | - | - | - | - | - | - | - |

Table 7 Sum of contributions and reactivity of atomic orbitals of carbon (2pz) in the formation of molecular orbitals in cobaltocene.

| Atomic orbital's of carbon | Sum of contribution of carbon orbital's | Sum of reactivity |
|---------------------------|----------------------------------------|------------------|
| 1C                        | 1.6332                                 | 0.6123           |
| 2C                        | 1.3124                                 | 0.7619           |
| 4C                        | 1.0519                                 | 0.9507           |
| 6C                        | 3.3601                                 | 0.2976           |
| 8C                        | 1.5142                                 | 0.6604           |
| 10C                       | 2.0235                                 | 0.4942           |
| 11C                       | 1.1071                                 | 0.9033           |
| 12C                       | 1.3382                                 | 0.7473           |
| 14C                       | 1.0473                                 | 0.9549           |

14C > 12C > 11C > 10C > 8C > 6C > 4C > 2C > 1C

Out of 59 molecular orbital Eigen values of nickelocene we shall discuss only 25 of them described in Table 8, for nickel orbitals and Table 10, for carbon orbitals. The first 14 MOs are Φ15-Φ16, Φ18-Φ20, Φ21 and Φ23-Φ30, are formed by various 3d and 2pz orbitals of (C\(_5\)H\(_5\))\(^-\). These orbitals with energies in the range of -9.9338 to -0.64271eV are the most stable molecular orbital between nickel and 2pz orbital of (C\(_5\)H\(_5\))\(^-\). The next eleven MOs i.e. Φ36-Φ40, Φ42-Φ43, Φ50, Φ53, Φ54 and Φ59 are formed by interaction of 4s, 4px, 4py and 4pz orbital of metal and 2pz orbital of carbon of (C\(_5\)H\(_5\))\(^-\). These MOs with energies in the range -0.56142 to -0.10622 eV are comparatively less stable. To examine the extent of involvement of 3d, 4s, 4p and 2pz orbitals in the formation of molecular orbitals the values of coefficient of each orbital are tabulated in Table 8.

The summation values given in Table 9 and plotted in Figure 7 show the total contributions from each atomic orbital. It is clearly indicated that 4py orbital has the maximum involvement out of 4s and 4p orbital and 3dyz orbital has the maximum involvement out of 3d orbitals. The sequence from the two series is given below:

4py > 4px > 4s > 4pz and 3dyz > 3d\(^2\)-\(y^2\) > 3dxy > 3dxz > 3d\(^2\)z

Sum of contributions of atomic orbitals of nickel in the formation of molecular orbitals of nickelocene is shown in Table 9 and Figure 7 that the sum of contributions of 3d\(^2\)z orbital in the formation of molecular orbitals is least out of the 3d orbitals and 4pz orbital is least out of 4s and 4p orbitals. Hence 3d\(^2\)z and 4pz are comparatively free for complex formations. The exact order of availability of atomic orbitals of Ni in nickelocene for complex formation is given below:

4pz > 4s > 4px and 3dyz > 3dx\(^2\)-\(y^2\) > 3dxy > 3dxz > 3d\(^2\)z

The summation values shown in Table 11 and Figure 8 clearly indicates that contribution of 2pz orbital of C has the maximum involvement out of the ten carbon atoms in (C\(_5\)H\(_5\))\(^-\). The sequence from the series are given below:
Table 8 Contributions of orbitals of nickel in the formation of molecular orbitals of nickelocene.

| MOs     | 4s   | 4p  | 4p  | 4p  | 3dx²-3y² | 3d²z² | 3dxy | 3dxz | 3dyz |
|---------|------|-----|-----|-----|----------|-------|-------|-------|-------|
| Φ15     | -    | -   | -   | -   | -        | -     | -     | -     | -     |
| Φ16     | -    | -   | -   | -   | -        | -     | 0.3209| 0.3365| 0.1991|
| Φ18     | -    | -   | -   | -   | -        | -     | -     | -     | -     |
| Φ19     | -    | -   | -   | -   | -        | -     | 0.3125| -     | -     |
| Φ20     | -    | -   | -   | -   | -        | 0.5297| -     | -     | -     |
| Φ21     | -    | -   | -   | -   | -        | 0.3029| -     | -     | -     |
| Φ23     | -    | -   | -   | -   | -        | 0.3279| -     | -     | -     |
| Φ24     | -    | -   | -   | -   | 0.3849  | 0.4986| 0.2011| -     | -     |
| Φ25     | -    | -   | -   | -   | 0.5232  | 0.3369| -     | 0.2396| 0.2782|
| Φ26     | -    | -   | -   | -   | 0.7408  | -     | -     | -     | -     |
| Φ27     | -    | -   | -   | -   | -        | 0.6697| -     | 0.2358| -     |
| Φ28     | -    | -   | -   | -   | 0.1702  | -     | -     | -     | -     |
| Φ29     | -    | -   | -   | -   | 0.2012  | -     | -     | -     | -     |
| Φ30     | -    | -   | -   | -   | 0.2979  | 0.1819| 0.4786| 0.3521| -     |
| Φ36     | -    | 0.5037| 0.5563| 0.2729| -       | -     | -     | -     | -     |
| Φ37     | 0.4088| 0.3254| 0.2960| -     | -       | -     | -     | -     | -     |
| Φ38     | 0.6732| 0.2423| 0.3695| -     | -       | -     | -     | -     | -     |
| Φ39     | -    | 0.7569| 0.3868| 0.3261| -       | -     | -     | -     | -     |
| Φ40     | -    | 0.2201| 0.3706| -     | -       | -     | -     | -     | -     |
| Φ42     | -    | 0.3487| 0.3318| -     | -       | -     | -     | -     | -     |
| Φ43     | -    | 0.6971| 0.7470| -     | -       | -     | -     | -     | -     |
| Φ50     | 0.7225| -    | -    | -     | 0.2979  | 0.1819| 0.4786| 0.3521| -     |
| Φ53     | -    | 0.3020| -    | 0.2283| -       | -     | -     | -     | -     |
| Φ54     | 0.6421| 0.4372| 0.5633| -     | -       | -     | -     | -     | -     |
| Φ59     | -    | 0.4436| 0.7620| 1.1256| -       | -     | -     | -     | -     |
| S       | 2.4466| 4.277| 4.3833| 1.9529| 1.8539  | 1.5768| 1.9095| 1.7671| 2.2815|

N.B: Orbitals having coefficient values above 0.10 have only been considered.

Table 9 Sum of contributions and reactivity of atomic orbital’s of nickel in the formation of molecular orbitals of nickelocene.

| Atomic orbital’s    | Sum of contributions of orbital’s of Ni | Sum of reactivity |
|---------------------|----------------------------------------|-------------------|
| 4s                  | 2.4466                                 | 0.4087            |
| 4p                  | 4.277                                  | 0.2338            |
| 4p                  | 4.3833                                 | 0.2281            |
| 4p                  | 1.9529                                 | 0.5212            |
| 3dx²-3y²            | 1.9439                                 | 0.5144            |
| 3dz²                | 1.5768                                 | 0.6342            |
| 3dxz                | 1.9095                                 | 0.5237            |
| 3dyz                | 1.7671                                 | 0.5657            |
| 3dxy                | 2.2815                                 | 0.4383            |

N.B: Orbitals having coefficient values above 0.10 have only been considered.

Sum of contributions of atomic orbitals of carbon (2pz) in the formation of molecular orbitals of nickelocene is shown in Table 11 and Figure 8 where the sum of contribution of C of 2pz orbital’s in the formation of molecular orbital’s are least out of the ten carbon atoms. Hence 3C are comparatively free for complex formations. The exact order of availability of carbon atom for complex formation is given below:

$^{12}C > ^{11}C > ^{10}C > ^{9}C > ^{8}C > ^{7}C > ^{6}C > ^{5}C > ^{4}C > ^{3}C > ^{2}C > ^{1}C$
for, 60 electrons of 30 molecular orbitals in cobaltocene and nickelocene. Each MOs has two electrons in cobaltocene and nickelocene but (the 30th MOs of cobaltocene and nickelocene have only one electron). The coefficient of atomic orbital cri is treated as Eigen vector value [24-26]. Value less than 0.1 have negligible contributions and are omitted in the calculations. Only 3d orbitals of metal and 2pz orbitals of carbon are considered in the calculation. The summation value of population analysis of these orbitals is shown in Table 12 of cobaltocene, and Table 13 of nickelocene. It is indicated that in MOs 1-19 of cobaltocene, in MOs 1-14 of nickelocene only 2s, 2py and 2px electrons of carbon have contributions in the formation of molecular orbital of cobaltocene and nickelocene hence are out of discussion. The summation value of population analysis of these orbitals to contribute electrons in the formation of molecular orbital is shown Tables 12 and 13 the result of the population analysis shows that only 2pz orbitals of carbon of (C₅H₅)⁻ and 3d orbitals of metal provide electrons to MOs of cobaltocene, and nickelocene.

Conclusion
We studied the electronic structure and geometry optimization of cobaltocene and nickelocene molecules using DFT/B3LYP with the basis set of 6-31G (d) calculations. We found that orbitals corresponding to the Eigen values (energy ranges -0.86738 to -0.56256 eV in cobaltocene and -9.90743 to -0.64271 eV in
Out of the 3d orbitals of cobaltocene and nickelocene molecules the 3dz orbitals have maximum involvement in the formation of molecular orbitals, whereas the 4s orbital out of 4s and 4p orbital of cobalt and 4py orbital out of 4s and 4p orbital of nickel show maximum involvement, in the order of 4s > 4pz > 4py > 4px and 3dyz > 3dxy > 3xz > 3dz^2 - y^2 in cobaltocene, and 4py > 4px > 4s > 4pz and 3dyz > 3dx^2 - y^2 > 3dxy > 3dz^2 in nickelocene. The total involvement in relation to the bonding between metal orbital derived from coefficient values are 24.2528 in cobaltocene and 22.8486 in nickelocene hence cobaltocene is more stable than nickelocene (formed between 3d orbitals of metal and 2pz orbitals of carbon). The less stable orbitals are in the energy ranges of -0.37685 to -0.03634 eV in cobaltocene and in -0.56142 to -0.10622 eV nickelocene. Eigenvectors of cobaltocene and nickelocene show that the first 12 MOs in cobaltocene 14 MOs of nickelocene are formed by various 3d orbitals of metal and 2pz orbital of (C_5H_5)− and the most stable MOs. The next 12 MOs in cobaltocene and 11 MOs of nickelocene are formed by the interaction of 4s and 4p orbitals of metal and 2pz orbital of carbon of (C_5H_5)− and these MOs are comparatively less stable orbitals.

### Table 11
Sum of contributions and reactivity of atomic orbitals of carbon (2pz) in the formation of molecular orbitals in nickelocene.

| Atomic orbital's of carbon | Sum of contribution of carbon orbital's | Sum of reactivity |
|---------------------------|----------------------------------------|-----------------|
| 1C                        | 0.8235                                 | 1.2143          |
| 2C                        | 0.6212                                 | 1.6098          |
| 3C                        | 1.2567                                 | 0.7957          |
| 4C                        | 1.0703                                 | 0.9344          |
| 5C                        | 2.1442                                 | 0.4667          |
| 10C                       | 1.5868                                 | 0.6302          |
| 11C                       | 0.9748                                 | 1.0259          |
| 12C                       | 0.7027                                 | 1.4231          |
| 13C                       | 1.164                                  | 0.8591          |
| 14C                       | 1.486                                  | 0.6729          |

### Table 12
The sum of contribution of electrons 3d orbitals of cobalt and 2pz orbitals of carbon in the formation of molecular orbitals of cobaltocene.

| MOs | No. of atomic orbitals | Eigenvector (c_i) | No. of electrons (n_i) | Net population (n_r) |
|-----|------------------------|-------------------|------------------------|----------------------|
| Φ20 | 2                      | 0.5855            | 4                      | 0.3344               |
| Φ21 | 3                      | 0.8773            | 6                      | 0.5154               |
| Φ22 | 2                      | 0.5907            | 4                      | 0.3470               |
| Φ23 | 10                     | 2.1549            | 20                     | 1.2661               |
| Φ24 | 8                      | 1.8713            | 16                     | 1.0994               |
| Φ25 | 6                      | 1.8031            | 12                     | 1.0593               |
| Φ26 | 8                      | 2.6812            | 16                     | 1.3475               |
| Φ27 | 10                     | 2.2936            | 20                     | 1.1527               |
| Φ28 | 11                     | 2.3559            | 22                     | 1.1829               |
| Φ29 | 9                      | 1.6489            | 18                     | 0.8279               |
| Φ30 | 12                     | 2.9759            | 12                     | 0.9391               |

Summation value of population analysis, (n_r) of occupied molecular orbital of cobaltocene is 10.0715.

### Table 13
The sum of contribution of electrons, 3d orbitals of nickel and, 2pz orbitals of carbon in the formation of molecular orbitals of nickelocene.

| MOs | No. of atomic orbitals | Eigenvector (c_i) | No. of electrons (n_i) | Net population (n_r) |
|-----|------------------------|-------------------|------------------------|----------------------|
| Φ15 | 3                      | 0.8252            | 6                      | 0.4884               |
| Φ16 | 2                      | 0.4285            | 4                      | 0.2537               |
| Φ18 | 1                      | 0.3605            | 2                      | 0.2134               |
| Φ19 | 1                      | 0.4718            | 2                      | 0.2793               |
| Φ20 | 1                      | 0.5297            | 2                      | 0.4163               |
| Φ21 | 3                      | 0.7034            | 6                      | 0.5529               |
| Φ23 | 4                      | 1.1606            | 8                      | 0.9122               |
| Φ24 | 6                      | 1.5789            | 12                     | 1.2410               |
| Φ25 | 5                      | 1.7438            | 10                     | 1.0979               |
| Φ26 | 2                      | 1.2357            | 4                      | 0.7780               |
| Φ27 | 4                      | 0.9055            | 8                      | 0.5701               |
| Φ28 | 7                      | 1.9303            | 14                     | 1.1425               |
| Φ29 | 8                      | 2.2311            | 16                     | 1.3206               |
| Φ30 | 12                     | 1.3426            | 24                     | 0.7947               |

Summation value of population analysis, (n_r) of occupied molecular orbital of nickelocene is 10.0609.
nickelocene. The total involvement in relation to the bonding between 2pz orbital of the ten carbon atoms of both ligands of (C\(_5\)H\(_5\)) of 15.986, and 15.529 in cobaltocene and nickelocene respectively, hence cobaltocene is more stable than nickelocene. As a summary, the total involvement of 3d, 4s and 4p orbitals of metal and 2pz orbitals of the ten carbon atoms of both ligands of (C\(_5\)H\(_5\))^− in cobaltocene and nickelocene respectively are 40.2388 and 38.3776 hence we can conclude that cobaltocene is more stable than nickelocene. This is in support of the results shown in terms of the parameters like dipole moment, HOMO-LUMO gap, ionization potential etc. discussed in the above. The population analysis shows that only 2pz orbitals of carbon of (C\(_5\)H\(_5\))− and 3d orbitals of metal provide electrons to MOs of cobaltocene and nickelocene.

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