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Iron, cobalt and Nickel -ligand bonding in metallocene: Differentiation between bonds Stability and reactivity

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Abstract— *The electronic structure and geometry optimization of ferrocene, cobaltocene and nickelocene molecules using DFT/B3LYP with the basis set of 6-31G (d) calculations. The Eigen values, Eigen vector and population analysis of the molecules show that the first 13 molecular orbitals in ferrocene, 12 in cobaltocene and 14 in nickelocene have contribution from 2pzorbitals of carbon of* $(C_5H_5)^-$ *and4s,4pand 3dorbitals of iron, cobalt or nickel, respectively. We found that the extents of involvement of metal orbitals in the three cases are different. In ferrocene the maximum involvement out of 4s and 4porbitals in the order 4pz >4py >4s > 4pxand out of 3d orbitals the order of involvement is 3dyz >3dxz >*$3d^2z$*>*$3dx^2-y^2$*>3dxy. The involvement of corresponding orbital in cobaltocene with respect to the 4sand 4porbitals is in the order of 4s >4pz >4py >4pxand in 3d orbitals the order is* $3dx^2-y^2$*>3dxz >*$3d^2z$*>*$3dx^2-y^2$ *and in the nickelocene molecule it is 4py >4p>4s >4pz and in 3d orbitals the order is 3dyz >*$3dx^2-y^2$*>3dxy >3dxz >*$3d^2z$*. The total involvement of 3d, 4s and 4porbitals of metal and 2pz orbitals of the ten carbon atoms of both ligands of* $(C_5H_5)^-$*in ferrocene, cobaltocene and nickelocene respectively are 42.2528, 40.2388 and 38.3776*

Keywords— ***Ferrocene, Cobaltocene, Nickelocene, Eigen vector, population analysis, Eigenvalues, atomic and molecular orbitals.***

I. 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 eigenvectors, Eigen values and population analysis of ferrocene,cobaltocene and nickelocene in order to study the extent of contribution of 3d, 4s and 4p orbital in the formation of MOs. The significant of Ferrocene and nickelocene are contribute of atomic orbitals in the formation of molecular orbital, chemical stability, mediator, asymmetric catalysis and more reactive material such as Ferrocene,Cobaltocene and Nickelocene as the commercially important for production of various metallocene, polymers and co-polymers. Such a quantitative study will provide correct information about the involvement of 4p orbital of Iron, cobalt andnickel in bonding will help to resolve the controversy raised by other workers [16-20].

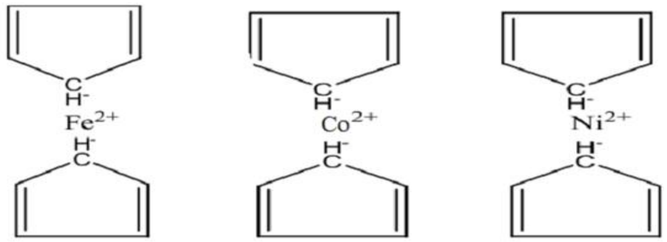

Fig.1: Stricture of Ferrocene, Cobaltocene and Nickelocene molecules respectively

II. 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 per-formed with in a finite set of basis 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 a combination of Beck's three-parameter exchange functional and Lee-Yang-Parr correlation functional with 6-31G (d) basis set.

These methods are found in Gaussian 03W program. B3LYP is a DFT method with hybrid functional that provides qualitative results at a lower cost than ab-initio methods with a comparable accuracy [21]. By using these methods we have optimized the energy, eigenvalues, eigenvector, population analysis, HOMO-LUMO energy gap, hardness, softness, electronegativity, visualize the HOMO and LUMO orbitals' of ferrocene,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]

III. RESULT AND DISCUSSION

This thesis is aimed to study the electronic structure and optimized geometry of ferrocene, 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 ferrocene, cobaltocene and nickelocene molecules are found through DFT/B3LYP with a basis set of 6-31G (d) calculations. The optimized structures of these three compounds are shown in Fig 1 A, B and C respectively for ferrocene, cobaltocene and nickelocene. The significant computed parameters are available in Tables 1, 2 and 3 including the bond lengths, bond angles and dihedral angles of these three compounds. The optimized bond length of C-C double and single bonds in ferrocene rings fall in the range 1.36-1.83˚A, cobaltocene 1.36-1.96 ˚A andnickelocene1.392-1.98 ˚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 ferrocene, cobaltocene and nickelocene and according to its bond length are in the order of C=C <C-C. From Tables 1, 2 and 3 we observe a slight difference in the bond lengths, bond angles and dihedral angles throughout the molecules of ferrocene, cobaltocene and nickelocene. This indicates that the aromatic iron atom in ferrocene, cobalt atom in cobaltocene and nickel atom in nickelocene are relatively stable metabolically.

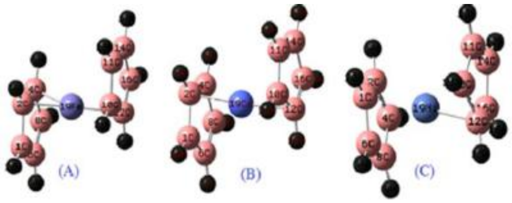

Fig.2: (A) Ferrocene (B) Cobaltocene (C) Nickelocene

Table.1: The selected bond lengths in˚A, bond angles and Dihedral angles of the optimized structure of ferrocene using DFT levels with B3LYP / 6-31G (d) basis set.

Entry	Bond length(˚A)	Entry	Bond angle (o)	Entry	Dihedral angle(o)
C1−C2	1.509	C6−C1−C2	109.511	C6−C1−C2−C4	0.027
C1−C6	1.509	C8−C6−C1	109.560	C8−C6−C1−C4	-0.027
C8−C6	3.359	C12−C10−C11	92.513	C10−C11−C14−C16	-85.951
C10−C11	1.509	C14−C10−C12	92.513	C16−C12−C10−C11	91.533

C10−C12	1.509	C10−C11−C14	85.520	Fe−C2−C1−C6	-67.604
C11−C14	1.359	C10−C12−C16	109.510		
C12−C16	1.359	Fe−C2−C1	88.83		
C2−C4	1.359				
C4−C8	1.47				
Fe−C2	1.825				

As shown in Figure 2.A and Table 1.the bond connectivity of Fe-$(C_5H_5)_2$ of the two ligands are asymmetrical. The iron atom in ferrocene is bonded with C_{12} atom with bond length of 1.954 (˚A) in one side of the ligand and $C_4$with bond length of 1.856(˚A) and with C_2atom of bond length 1.856 (˚A) on the opposite side. The Fe-C bond length on the two sides of the ligand have small variations due to the double bond ofC_2-C_4 which possess more energy to attract iron atom to-wards itself than the single bond on the other side,hence$Fe-C_2$and$Fe-C_4$ bonds measure shorter distance than the bond in$Fe-C_{12}$.In the ferrocene molecule the iron atom is located between the two ligands but inclined by -67.604ofrom the plane of the cyclopentadienyl and the two ligands are almost parallel but with a slide of one from the other by a center of mass separation of 1.67˚A.

Table.2: The selected bond length˚A, bond angles and Dihedral angles of the optimized Structure of cobaltocene using DFT levels with B3LYP / 6-31G (d) basis set.

Entry	Bond length(˚A)	Entry	Bond angle (o)	Entry	Dihedral angle(o)
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	109.560	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				

As shown in Figure 2.B and Table 2.the bond connectivity of Co -$(C_5H_5)_2$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 withC_2atom of bond length 1.969 (˚A) in one side of the ligand and with $C_{12}$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 -80.623omeasured 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

Table.3: The selected bond length˚A, bond angles and Dihedral angles of the optimized Structure of nickelocene using DFT levels with B3LYP / 6-31G (d) basis set.

Entry	Bond length(˚A)	Entry	Bond angle (o)	Entry	Dihedral angle(o)
C1−C2	1.424	C1−C2−C4	106.850	C6−C1−C2−C4	-174.834
C2−C4	1.419	C2−C1−C6	108.850	C2−C1−C6−C8	-8.963
C1−C6	1.448	C1−C6−C8	107.560	C1−C2−C4−C8	6.050
C6−C8	1.391	C10−C11−C14	93.450	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	105.110	C10−C11−C14−C16	82.950
C11−C14	1.366	Ni−C12−C10	72.433	C14−C16−C12−Ni	-67.377
C12−C16	1.427				
Ni−C2	1.976				

Figure 2.B and Table 3.The bond connectivity of Ni-(C_5H_5)$_2$of the two ligands isasymmetrical.The nickel atom in nickelocene is bonded withC_{12} 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 electrons and low spin arrangement with six 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 -67.377°as measured from the plane of the cyclopentadienyl 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 ferrocene, 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 others.

In the calculations of Mullikan charge distributions of ferrocene, cobaltocene and nickelocene 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).

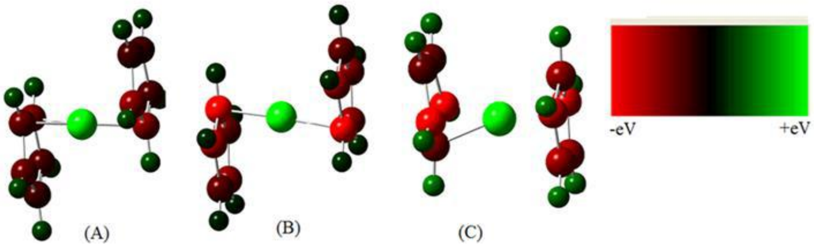

Fig.3:The Milliken charge distributions of ferrocene, cobaltocene and nickelocenerespectively.

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 molecules 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 4

Table.4: Important parametric properties of the molecules calculated at the DFT/B3LYPLevels in 6-31G (d) basis set.

Molecular properties	**ferrocene**	**cobaltocene**	**nickelocene**
RB-HF-LYP (eV)	-1896.275	-1769.5679	-1650.740
εHOMO(eV)	-0.6491	-0.6452	-0.6427
εLUMO(eV)	-0.5628	-0.5626	-0.5614
εLUMO−εHOMO energy gap (eV)	0.0863	0.0826	0.0813
Ionization potential(I in eV)	0.6491	0.6452	0.6427
Electron affinity(A in eV)	0.5628	0.5626	0.5614
Global hardness (η in eV)	0.0431	0.04129	0.04065

Global softness (Sin eV)	23.1803	24.216	24.6030
Electro negativity (χ in eV)	0.60591	0.6039	0.6021
Chemical potential (µin eV)	-0.6059	-0.6039	-0.6021
Dipole moment (µin Debye)	1.464	1.695	1.931
Mullikan charge distributions (M.C.D in e)	±1.093	±1.13	±1.692

DFT/B3LYP level the HOMO energy of ferrocene is -0.6491 eV which is slightly more negative than the cobaltocene -0.6427 eV and nickelocene of -0.6427 eV and the LUMO energy of ferrocene is -0.5628 eV, cobaltocene -0.5626 and nickelocene -0.56142 eV. The HOMO-LUMO gap of ferrocene, cobaltocene and nickelocene are 0.0863, 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 ferrocene molecule shows relatively high energy gap value and the data here suggested that ferrocene is relatively less reactive and more stable than cobaltocene and nickelocene molecules. The most stable MO energy of ferrocene, cobaltocene and nickelocene are respectively -254.0054, -277.5151 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 reactions. This description also supports for ferrocene, cobaltocene and nickelocene molecules; ferrocene is harder than cobaltocene and nickelocene. In Table 4 the HOMO-LUMO gap, as a characteristic of reactivity, shows ferrocene has lower chemical reactivity comparing to cobaltocene and nickelocene molecules. Absolute hardness and softness are important properties to measure the molecular stability and reactivity. Itis 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 ferrocene molecule, the HOMO-LUMO energy gap and hardness, η is larger comparing to cobaltocene and nickelocene molecules. The dipole moments and Mullikan charge ranges as displayed in Table 4.Nickelocene would have more charge than the ferrocene and 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 nickelocene is 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.

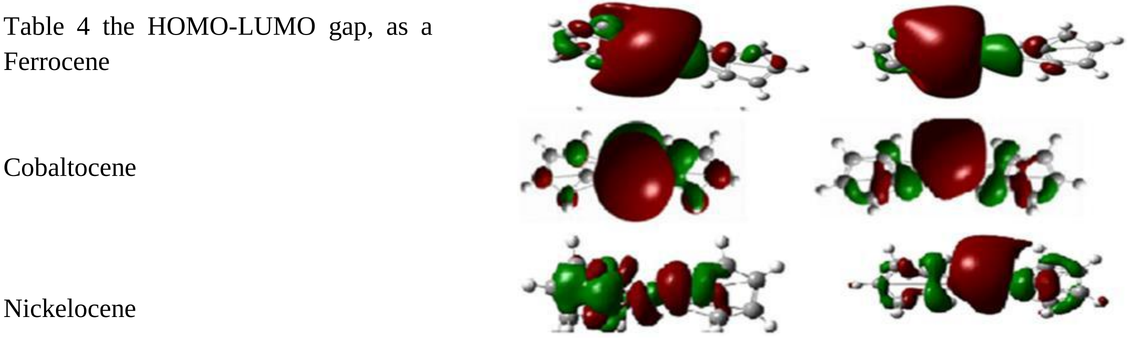

Fig.4: The left side of HOMO and the right side of LUMO surfaces of ferrocene, cobaltocene and nickelocene compounds, down of the column respectively.

The abovefigure shows the visualized structures of ferrocene, cobaltocene and nickelocene show the population of electrons on their orbitals. The HOMO orbitals represented by green color, whereas for LUMO 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 ferrocene, 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 ferrocene, cobaltocene and nickelocene are formed by linear combination of fifty AOs of two $(C_5H_5)^-$and nine orbital of iron, cobalt and nickel. These fifty-nine AOsχ1to χ59on LCAO approximation form same number of MOs, Φ1 to Φ59. The AOs χ1toχ40for 2s, 2px, 2py, 2pzof 1C to 10C, χ41 toχ49 for4s, 4px, 4py, 4pz, $3dx^2-y^2$, $3d^2z$, 3dxy, 3dxz, 3dyzof 11M andχ50to χ59for 1s of 12H to21H respectively, where M = Fe, Co, and Ni for ferrocene, cobaltocene and nickelocene respectively. The 2s, 2pxand 2pyorbitals of each carbonatom of $(C_5H_5)^-$are involved in the formation of σ bond between C-C and C-H. The orbitalsinvolved in σ bond hence shall remain out of discussion. The 2pz orbitals of ten carbons and nine orbitals of iron , cobalt or nickel i.e. In total nineteen orbitals are relevant to our discussion in respect of bonding between iron, cobalt or nickel orbitals and 2pzorbital of (C_5H_5)-. These atomic orbitalsareχ4, χ8, χ12, χ16, χ20, χ24, χ28, χ32, χ36andχ40 of carbon and χ41to χ49of iron, cobalt or nickel. The coefficients of these orbitals are the eigenvector values of χ[21].They express the forms of MOs i.e. the extent of involvement of χ in the formation of Φ. In order to examine the contribution of various atomic orbitals in the formation of molecular orbitals. The Eigen vector analysis has been made and studied and data are given tables 5 to 15 respectively. The coefficients of these orbital are the Eigen vector values of, χ which have been evaluated by density functional method using Gaussian-03 software. They express the form of molecular orbital that is the extent of involvement of χ in the formation of Φ. The calculated Eigen vector values of atomic orbitals of Fe , Co and Ni in the formation of molecular orbitals in ferrocene, cobaltoceneand nickelocene in Table 5, 6, 9 , 10, 13 and 14 respectively and the calculated Eigen vector values of 2pzorbital of carbon are given in Table 7, 8, 11, 12,15 and 16. Table 6,8and14 is summation of Eigen vector values of ferrocene, cobaltocene and nickelocene. Negative, Zero and near zero coefficient values are negligible contributions [21, 23] of electrons and have been excluded from the Tables.

Out of the 59 molecular orbitals of ferrocene molecule only 22 molecular orbitals shall be discussed as described in Table 5 for Iron orbital and Table 7.For Carbon orbital. In ferrocene the first 13 molecular orbitals Φ18,Φ20,Φ22,Φ23−Φ31 and Φ35are formed by only two atomic orbitals, 3d orbital of iron and2pzorbital $(C_5H_5)^-$. These orbitals are the most stable molecular orbital and have their energies in the range -2.03849 to -0.54008eV. The next nine molecular orbital Φ36−Φ37, Φ40−Φ41, Φ43, Φ50−Φ51, Φ54−Φ55haveformed from contribution of vacant 4s, 4px, 4pyand 4pzorbital of the iron and 2pzorbital of carbon. These MOs are comparatively less stable and have their energies between -0.53616and -0.107076 eV. To examine the extent of involvement of 3d, 4s and 4porbital in the formation of molecular orbitals the values of coefficient of each orbital have been added as shown in Table 6.

Table.5: Contributions of orbitals of iron in the formation of molecular orbitals of ferrocene. N.B; orbitals having coefficient values above 0.1 have only been considered.

MOs	4s	4px	4py	4pz	$3dx^2$-y^2	$3dz^2$	3dxy	3dxz	3dyz
	χ41	χ42	χ43	χ44	χ45	χ46	χ47	χ48	χ49
Φ18	-	-	-	-	0.2947	0.2991	-	-	-
Φ20	-	-	-	-	-	-	-	-	0.2361
Φ22	-	-	-	-	-	-	-	0.2728	-
Φ23	-	-	-	-	0.4708	0.1156	-	0.2893	0.2288
Φ24	-	-	-	-	0.1041	-	0.2847	0.4762	0.2718
Φ25	-	-	-	-	0.6472	-	-	-	0.3147
Φ26	-	-	-	-	-	0.2269	0.8185	-	0.1004
Φ27	-	-	-	-	0.1063	0.5776	0.2565	-	0.4672

Φ28	-	-	-	-	0.3760	-	-	-	0.1352
Φ29	0.1452	-	-	-	0.1367	0.5383	-	-	-
Φ30	-	-	-	-	-	0.3496	-	0.5271	0.3891
Φ31	-	-	-	-	-	-	-	0.4573	0.4577
Φ35	-	-	-	-	0.2392	-	-	-	-
Φ36	-	0.7335	0.6722	0.4698	-	-	-	-	-
Φ37	0.5031	0.7533	0.6888	-	-	-	-	-	-
Φ40	0.7981	-	0.2865	-	-	-	-	-	-
Φ41	-	-	0.2780	0.7412	-	-	-	-	-
Φ43	-	-	-	0.3154	-	-	-	-	-
Φ50	0.9232	-	-	0.7275	-	-	-	-	-
Φ51	-	-	0.3489	0.9974	-	-	-	-	-
Φ54	-	0.2810	0.3923	0.6228	-	-	-	-	-
Φ55	0.5802	0.3805	0.4346	-	-	-	-	-	-

Table.6: Sum of contributions and reactivity of atomic orbital's of iron in the formation of molecular orbitals of ferrocene

Atomic orbital's of Fe	Sum of contributions of orbital's of Fe	Sum of reactivity
4s	2.9498	0.3390
4p x	2.1483	0.4655
4p y	3.101	0.3225
4p z	3.8741	0.2581
3dx2−y2	2.375	0.4215
3d2z	2.1071	0.4746
3dxy	1.3597	0.7356
3dxz	2.0227	0.4944
3dyz	2.601	0.3845

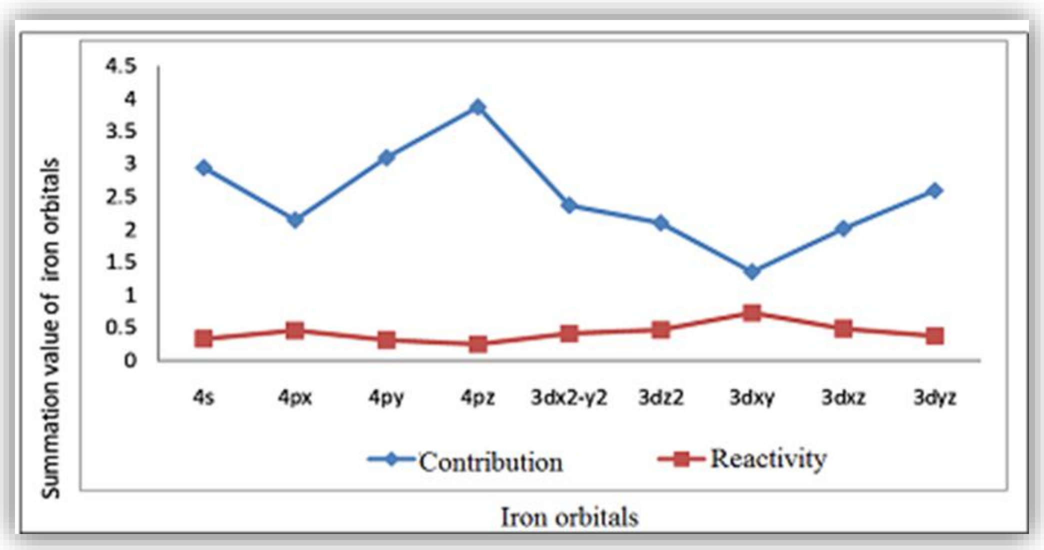

Fig.5: Sum of contributions and reactivity of atomic orbitals of, iron in the formation of molecular orbitals of ferrocene.

The summation of contributions of iron orbitals are placed in Table 6 and the total contribution from each atomic orbital is shown in Figure 5. It is clearly indicated that 4pzorbital has the maximum involvement out of 4sand

4porbitals, and 3dyz orbital has the maximum involvement out of the 3dorbital. The exact order of availability of atomic orbital of Fe in ferrocene for contributions of atomic orbitals for the formation of molecular orbital is given below;

4pz >4py >4s > 4px and

$3dyz > 3dx^2-y^2 > 3d^2z > 3dxz > 3dxy$ Eq (1)

Sum of contributions of atomic orbitals of iron in the formation of molecular orbitals of ferrocene is shown in Table 6, in here the sum of contributions of 3dxyorbital in the formation of molecular orbitals is least out of the 3dorbitals and 4pxorbital in the formation of molecular orbitals is least out of 4s and 4p orbitals. Hence 3dxyand 4pxare comparatively free forcomplex formations. The exact order of availability of atomic orbital of Fe in ferrocene for complex formation is given below;

4px >4s >4py >4pzx and

$3dxy > 3dxz > 3d^2z > 3dx^2-y^2 > 3dyz$ Eq (2)

Table.7: Contributions of 2pz orbitals of carbon atoms in $(C_5H_5)^-$ in the formation of molecular orbitals of ferrocene. Orbitals having coefficient values above 0.1 have only been considered

MOs	**1C**	**2C**	**4C**	**6C**	**8C**	**10C**	**11C**	**12C**	**14C**	**16C**
	$\chi 4$	$\chi 8$	$\chi 12$	$\chi 16$	$\chi 20$	$\chi 24$	$\chi 28$	$\chi 32$	$\chi 36$	$\chi 40$
Φ18	-	-	-	-	0.2872	-	-	-	-	-
Φ20	0.3559	-	-	-	-	-	-	-	-	0.2361
Φ22	-	0.2261	-	-	-	-	-	0.3794	-	-
Φ23	-	0.2151	-	0.2796	-	-	0.2336	-	-	0.2841
Φ24	0.2133	-	-	0.1005	0.1385	0.1852	-	0.2312	0.1199	0.1272
Φ25	0.2062	-	0.2511	-	-	0.1770	-	0.1981	-	0.1486
Φ26	-	-	0.1668	0.1949	0.1218	0.1761	-	-	-	0.1848
Φ27	-	0.2685	-	-	-	-	0.2273	-	-	-
Φ28	-	0.2347	0.2169	0.1190	0.1844	0.3799	0.2591	0.2011	0.3185	-
Φ29	-	0.3310	0.1780	0.1828	0.2399	-	0.2523	-	0.1163	0.2543
Φ30	0.2886	-	0.3015	-	-	0.2907	-	0.2767	-	-
Φ31	0.2644	0.3474	-	-	0.3104	-	0.3409	0.2797	0.3116	-
Φ35	0.4567	0.4381	-	-	0.3623	-	0.4564	0.4820	0.3912	0.2243
Φ36	0.2629	-	-	-	-	-	-	-	-	0.2243
Φ37	-	0.2973	-	-	-	-	0.2673	0.2552	-	-
Φ40	-	-	0.3089	-	-	-	-	-	-	0.3653
Φ41	0.2114	-	0.2234	-	-	-	-	-	-	0.2387
Φ43	-	-	-	0.2661	-	-	-	-	-	-
Φ50	-	-	-	0.4338	-	-	-	-	-	0.3828
Φ51	-	-	-	0.3149	-	-	-	-	-	0.3416
Φ54	-	-	-	-	0.1856	-	-	-	-	-
Φ55	-	-	-	-	-	-	0.3004	-	-	-

Table.8: Sum of contribution values and reactivity of atomic orbitals of carbon in the formation of molecular orbitals of ferrocene

Atomic orbital's of carbon	**Sum of contribution of carbon orbital's**	**Sum of reactivity**
1C	2.2594	0.4426
2C	2.3582	0.4241
4C	1.6466	0.6073
6C	1.8916	0.0.4589
8C	1.8301	0.5465
10C	1.2089	0.8274
11C	2.3373	0.4278

12C	2.3034	0.4341
14C	1.2575	0.7955

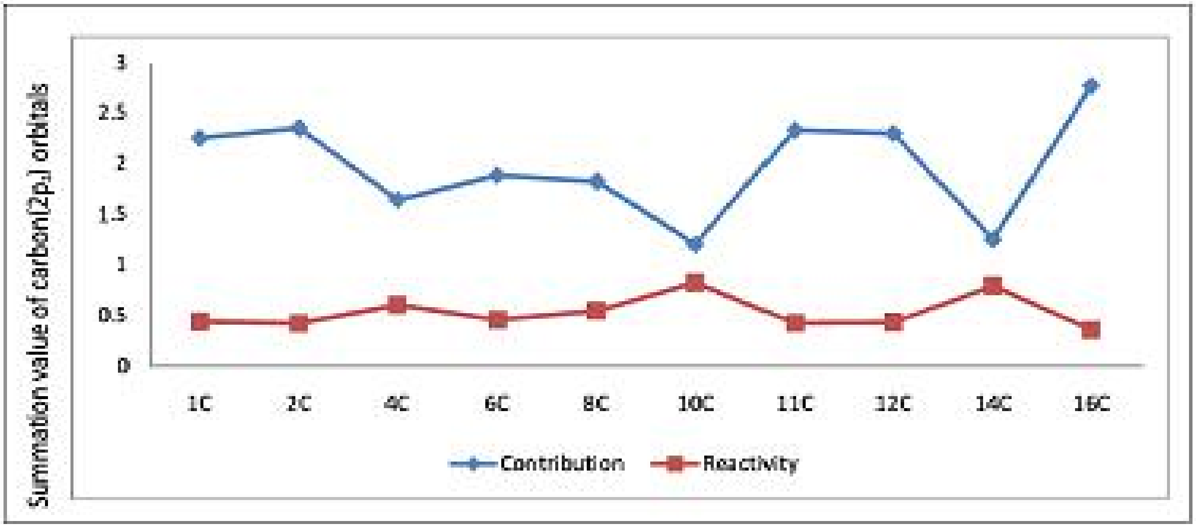

Fig.6: Sum of contributions and reactivity of atomic orbitals of carbon in the formation of molecular orbitals of ferrocene.

Table 8 and Figure 6 show the summation values where the total contributions from each atomic orbital of carbon clearly indicates that eigenvector value of 2pz orbital of 16Chas the maximum involvement out of the ten carbon atoms in both $(C_5H_5)^-$ ligands. The sequences from the series are as below:

16C >2C >11C >12C >1C >6C >8C >4C >14C >10C. Eq (3)

Sum of contributions of atomic orbitals of carbon (2pz) in the formation of molecular orbitals of ferrocene is shown in Table 8.And Figure 6.where the 10C contributions in the formation of molecular orbitals are least out of the ten carbon atoms. Hence 10C is comparatively free for complex formation. The sequence from the series is shown below:

10C >14C >4C >8C >6C > 1C >12C >11C >2C >16C. Eq (4)

Out of 59 molecular orbital Eigen values of cobaltocene we shall discuss only 24 of them described in Table 9.for cobalt orbitals and Table 11.for carbon orbitals. The first 12MOsare Φ20 −Φ31vformed by various 3d orbital of cobalt and 2pz orbital of $(C_5H_5)^-$.These orbital with energies in the range of -0.86738 to -0.56256 eV are the most stable molecular orbitals. The next 12 molecular orbitals areΦ36−Φ38, Φ41−Φ42, Φ46−Φ47, Φ50−Φ51; Φ54−Φ55 and Φ56 have contributions from vacant 4s, 4px, 4pyand 4pzorbital of cobalt and 2pz orbital of carbon. These MOs with energies between -0.37685 to -0.03634eV are comparatively less stable. To examine the extent of involvement of 3d, 4s, and, 4porbital in the formation of molecular orbital the values of coefficient of each orbital have been added to see the total involvement in all the 24 molecular orbital shown in Table 10.

Table.9: Contributions of orbitals of cobalt in the formation of molecular orbitals of cobaltocene.N.B; Orbitals having coefficient values above 0.10 have only been considered.

MOs	**4s**	**4p x**	**4py**	**4pz**	**$3dx^2$-y^2**	**$3dz^2$**	**3dxy**	**3dxz**	**3dyz**
	χ41	χ42	χ43	χ44	χ45	χ46	χ47	χ48	χ49
Φ20	-	-	-	-	-	-	-	-	0.2124
Φ21	-	-	-	-	-	-	-	0.2335	0.3224
Φ22	-	-	-	-	-	-	0.2113	-	-
Φ23	-	-	-	-	0.2507	0.4737	0.2664	0.2327	0.1436
Φ24	-	-	-	-	0.5537	0.1378	0.4186	0.1448	0.2731
Φ25	0.1198	-	-	-	-	0.5281	-	0.3033	0.5717
Φ26	-	-	-	-	0.2652	0.1081	0.5281	0.3717	0.3035
Φ27	-	-	-	-	0.1445	-	0.2931	0.2063	-

Φ28	-	-	-	-	0.1103	0.1402	0.2339	-	0.2297
Φ29	-	-	-	-	-	0.2052	0.2116	0.1243	-
Φ30	-	-	-	-	-	0.5131	0.2416	0.3996	0.1363
Φ31	-	-	-	-	0.3741	-	-	0.3523	0.4225
Φ36	0.3346	0.9288	-	0.4070	-	-	-	-	-
Φ37	0.3259	-	0.8777	0.5650	-	-	-	-	-
Φ38	0.6188	-	-	0.2691	-	-	-	-	-
Φ41	0.3195	-	0.3626	0.4823	-	-	- -	-	-
Φ42	0.3148	-	0.3549	0.3479	-	-	-	-	-
Φ46	0.2767	0.3026	-	0.3002	-	-	-	-	-
Φ47	0.3329	-	0.2698	0.2911	-	-	-	-	-
Φ50	0.7259	-	0.2913	0.3794	-	-	-	-	-
Φ51	0.5741	0.5317	0.3413	0.7871	-	-	-	-	-
Φ54	-	0.2380	0.2945	0.2227	-	-	-	-	-
Φ55	0.3738	0.2889	0.3878	-	-	-	-	-	-
Φ56	0.2297	-	-	-	-	-	-	2.3685	-

Table.10: 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
$3dx^2-y^2$	1.6985	0.58875
$3d^2_z$	2.1062	0.4748
$3d_{xy}$	2.4046	0.4159
$3d_{xz}$	2.3685	0.4222
$3d_{yz}$	2.6152	0.3824

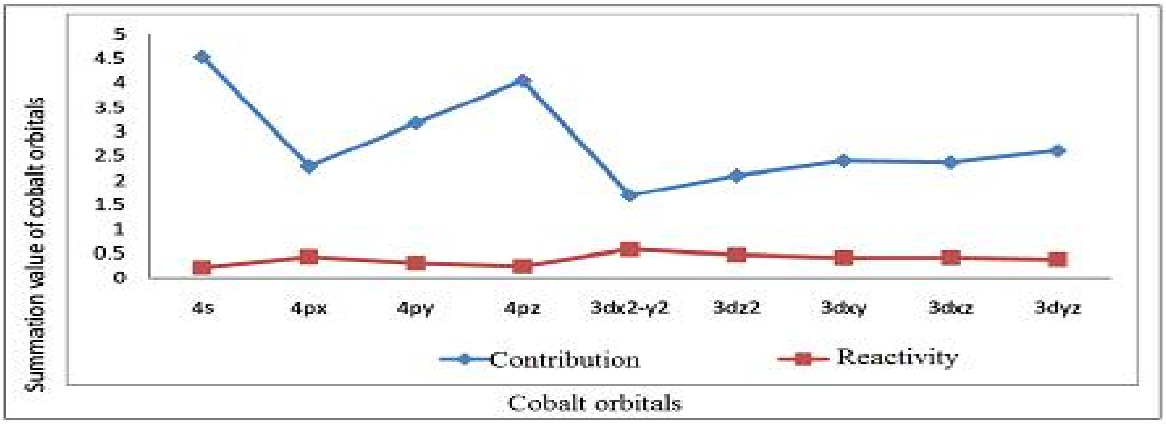

Fig.7: Sum of contributions and reactivity of atomic orbital's of, Co in the formation of molecular orbitals of cobaltocene.

The summation values given in Table 10.and plotted in Figure 7.show the total contributions from each atomic orbital. It is clearly indicated that 4sorbital has the maximum involvement out of 4sand 4porbital and 3dyzorbital has the maximum involvement out of 3dorbitals. The sequence from the series is given below:

4s >4pz >4py >4px and

$3dyz>3dxy>3dxz>3d2z>3dx^2-y^2$.Eq (5)

Sum of contributions of atomic orbitals of cobalt in the formation of molecular orbitals of cobaltocene is shown in Table 10.And Figure 7.That the sum of contributions of $3dx^2{-}y^2$orbital in the formation of molecular orbitals is least out of the 3dorbitals and 4pxorbital is least out of 4sand 4porbitals. Hence $3dx^2{-}y^2$ and 4px are comparatively free for complex formations. The exact order of availability of atomic orbitals of Coin cobaltocene for complex formation is given below;4px>4py >4pz >4s and
$3dx^2{-}y^2 > 3dz^2 > 3dxz > 3dxy > 3dyz$. Eq (6)

Table.11: Contributions of 2pzorbitals of carbon atoms in $(C_5H_5)^-$ in the formation of molecular orbitals of cobaltocene. N.B; orbital having coefficient value above, 0.10 have only been considered

MOs	**1C**	**2C**	**4C**	**6C**	**8C**	**10C**	**11C**	**12C**	**14C**	**16C**
	$\chi4$	χ^{8}	χ^{12}	χ^{16}	χ^{20}	χ^{24}	χ^{28}	χ^{32}	χ^{36}	χ^{40}
Φ20	0.3731	-	-	-	-	-	-	-	-	-
Φ21	-	-	-	-	-	0.3214	-	-	-	-
Φ22	-	-	-	-	-	-	-	0.3794	-	-
Φ23	0.1117	-	-	0.2610	-	0.1332	-	0.1701	0.1118	-
Φ24	-	-	0.1153	-	-	0.1220	-	0.1060	-	-
Φ25	-	-	-	0.1338	-	0.1464	-	-	-	-
Φ26	-	0.1818	-	0.1756	-	-	-	-	-	0.1472
Φ27	-	0.3281	0.2463	0.2716	0.2181	0.2369	0.2113	-	-	0.1374
Φ28	0.2825	-	0.2548	0.1501	0.1591	0.2836	0.2755	-	0.2362	-
Φ29	-	0.2024	0.1605	-	0.1336	0.1537	0.1515	-	-	0.3061
Φ30	0.2899	-	0.2750	0.1276	0.2474	0.2537	-	0.2649	0.1558	0.2073
Φ31	0.2835	0.3653	-	0.2853	0.2495	-	0.2476	-	-	-
Φ36	-	0.2348	-	-	-	-	-	0.2304	-	-
Φ37	-	-	-	0.2413	-	-	0.2212	-	-	-
Φ38	-	-	-	0.5191	-	0.1146	-	0.1874	0.2835	-
Φ41	0.2925	-	-	0.5471	0.2847	-	-	-	-	-
Φ42	-	-	-	-	-	-	-	-	-	-
Φ46	-	-	-	-	-	0.2580	-	-	0.260	-
Φ47	-	-	-	0.3743	-	-	-	-	-	-
Φ50	-	-	-	0.2733	-	-	-	-	-	0.2233
Φ51	-	-	-	-	-	-	-	-	-	0.5771
Φ54	-	-	-	-	0.2218	-	-	-	-	-
Φ55	-	-	-	-	-	-	-	-	-	-
Φ56	-	-	-	-	-	-	-	-	-	-

Table.12: 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

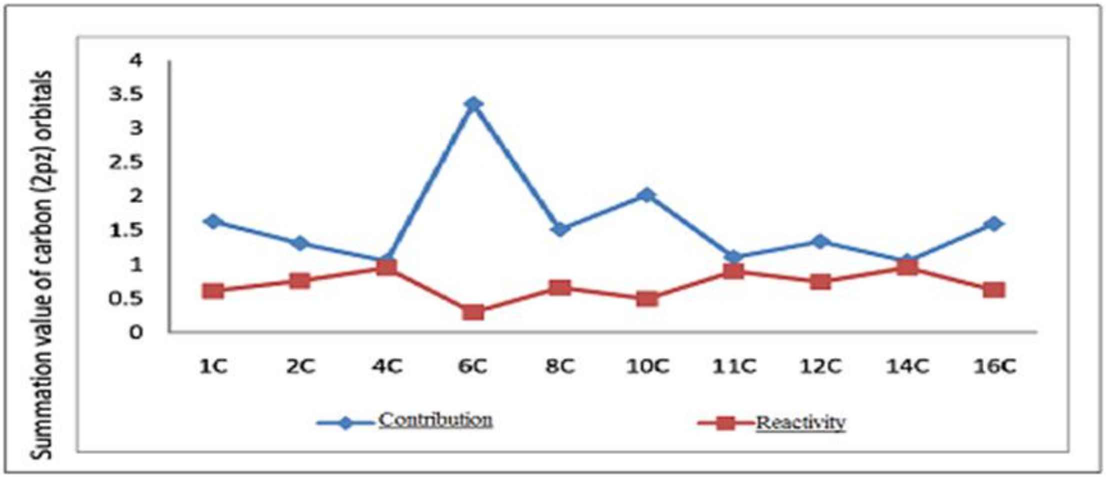

Fig.8: Sum of contributions and reactivity of atomic orbitals of carbon in the formation of molecular orbitals of cobaltocene.

The summation values shown in Table 12.And Figure 8.clearly indicates that contribution of 2pzorbital of 6Chas the maximum involvement out of the ten carbon atoms in $(C_5H_5)^-$The sequence from the three series are given below:
6C >10C >1C >16C >8C >12C >2C >11C >4C >14C. Eq (7)

Sum of contributions of atomic orbitals of carbon (2pz) in the formation of molecular orbitals of cobaltocene is shown in Table 12.And Figure 8.where the sum of contribution of 14C of 2pzorbital's in the formation of molecular orbital's are least out of the ten carbon atoms. Hence 14C are comparatively free for complex formations. The exact order of availability of carbon atom for complex formation is given below:
14C>4C >11C >2C >12C >8C >16C >1C >10C >6C. Eq (8)

Out of 59 molecular orbital Eigen values of nickelocene we shall discuss only 25 of them described in table 12.For nickel orbitals and table 15.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_5H_5)- These orbitals with energies in the range of -9.9338 to -0.64271eV are the most stable molecular orbital between nickel and2pzorbital of $(C_5H_5)^-$. The next eleven MOs i.e.Φ36−Φ40, Φ42−Φ43, Φ50, Φ53, Φ54andΦ59are formed by interaction of 4s, 4px, 4pyand 4pz orbital of metal and 2pz orbital of carbon of $(C_5H_5)^-$. 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, 4pand 2pz orbitals in the formation of molecular orbitals the values of coefficient of each orbital are tabulated in table 14.

Table.13: Contributions of orbitals of nickel in the formation of molecular orbitals of nickelocene. N.B; Orbitals having coefficient values above 0.10 have only been considered.

MOs	4s	4p x	4py	4pz	$3dx^2$-y^2	$3dz^2$	3dxy	3dxz	3dyz
	χ41	χ42	χ43	χ44	χ45	χ46	χ47	χ48	χ49
Φ15	-	-	-	-	-	-	-	0.3209	0.3365
Φ16	-	-	-	-	-	-	-	0.2294	0.1991
Φ18	-	-	-	-	-	-	0.3605	-	-
Φ19	-	-	-	-	-	-	0.3125	-	-
Φ20	-	-	-	-	0.5297	-	-	-	-
Φ21	-	-	-	-	0.3029	-	-	-	-
Φ23	-	-	-	-	0.3279	-	-	-	0.1838
Φ24	-	-	-	-	-	-	0.3849	0.4986	0.2011
Φ25	-	-	-	-	0.5232	0.3369	-	0.2396	0.2782
Φ26	-	-	-	-	-	0.7408	-	-	0.4949
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	-	-	-	-	-	-	-	-
Φ53	-	0.3020	-	0.2283	-	-	-	-	-
Φ54	0.6421	0.4372	0.5633	-	-	-	-	-	-
Φ59	-	0.4436	0.7620	1.1256	-	-	-	-	-

Table.14: Sum of contributions and reactivity of atomic orbital's of nickel in the formation of molecular orbitals of nickelocene.

Atomic orbital's of Ni	Sum of contributions of orbital's of Ni	Sum of reactivity
4s	2.4466	0.4087
$4p_x$	4.277	0.2338
$4p_y$	4.3833	0.2281
$4p_z$	1.9529	0.5121
$3dx^2{-}y^2$	1.9439	0.5144
$3d^2_z$	1.5768	0.6342
$3d_{xy}$	1.9095	0.5237
$3d_{xz}$	1.7671	0.5657
$3d_{yz}$	2.2815	0.4383

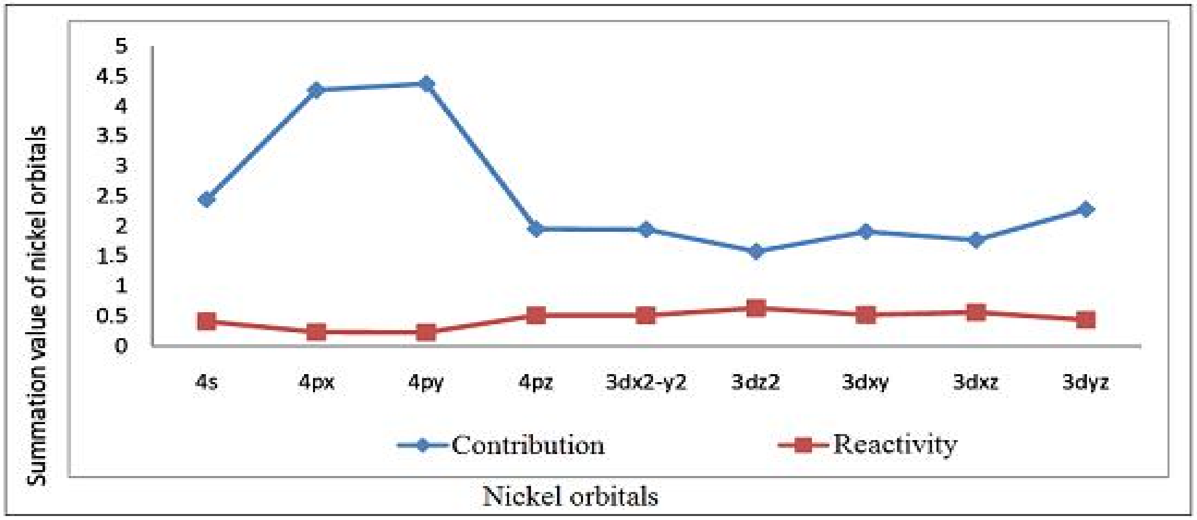

Figure 9: Sum of contributions and reactivity of atomic orbital's of nickel in the formation of molecular orbitals of nickelocene.

The summation values given in Table 14.And plotted in Figure 9.show the total contributions from each atomic orbital. It is clearly indicated that 4pyorbital has the maximum involvement out of 4sand 4porbital and 3dyzorbital has the maximum involvement out of 3dorbitals. The sequence from the two series is given below:

$$4py > 4px > 4s > 4pz \text{ and}$$

$$3dyz > 3dx^2{-}y^2 > 3dxy > 3dxz > 3d^2z. \text{ Eq (9)}$$

Sum of contributions of atomic orbitals of nickel in the formation of molecular orbitals of nickelocene is shown in Table 14.And Figure 9.That the sum of contributions of 3d^{2}zorbital in the formation of molecular orbitals is least out of the 3dorbitals and 4pzorbital is least out of 4sand 4porbitals. Hence 3d^{2}zand 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>4py and

3dyz>3dxz>3dxy>3dx^2−y^2>3dyz Eq (10)

Table.15: Contributions of 2pz orbitals of carbon atoms in (C_5H_5)$^-$ in the formation of molecular orbitals of nickelocene. N.B; orbital having coefficient value above, 0.10 have only been considered

MOs	**1C**	**2C**	**4C**	**6C**	**8C**	**10C**	**11C**	**12C**	**14C**	**16C**
	$\chi4$	χ^{8}	χ^{12}	χ^{16}	χ^{20}	χ^{24}	χ^{28}	χ^{32}	χ^{36}	χ^{40}
Φ15	-	-	-	-	-	-	-	-	0.1678	-
Φ16	-	-	-	-	-	-	-	-	-	-
Φ18	-	-	-	-	-	-	-	-	-	-
Φ19	-	-	-	-	-	-	-	-	-	-
Φ20	-	-	-	-	-	-	-	-	-	-
Φ21	-	-	-	0.2019	-	-	-	-	-	0.1986
Φ23	-	-	-	0.2182	-	-	0.1815	-	-	-
Φ24	-	-	-	-	0.1692	-	-	0.1544	-	0.1707
Φ25	-	-	-	-	-	-	-	-	-	0.2018
Φ26	-	-	-	-	-	-	-	-	-	-
Φ27	-	-	0.2142	-	-	0.1666	-	-	-	-
Φ28	0.2818	-	0.3050	-	0.2252	0.4088	0.2304	-	0.3089	-
Φ29	-	0.4189	0.2037	0.2561	0.2707	-	0.3600	-	0.2006	0.3209
Φ30	0.3293	-	0.3232	0.1812	0.1505	0.3096	-	0.3219	0.1864	0.2300
Φ36	-	-	0.2106	-	-	0.2172	-	-	0.3003	-
Φ37	0.2124	0.2023	-	-	-	0.2123	-	-	-	-
Φ38	-	-	-	-	-	-	-	-	-	-
Φ39	-	-	-	-	-	-	0.2029	0.2264	-	-
Φ40	-	-	-	-	0.4239	-	-	-	-	-
Φ42	-	-	-	-	0.2725	-	-	-	-	-
Φ43	-	-	-	-	-	-	-	-	-	-
Φ50	-	-	-	-	0.4095	-	-	-	-	0.3640
Φ53	-	-	-	0.2129	-	-	-	-	-	-
Φ54	-	-	-	-	-	0.2723	-	-	-	-
Φ59	-	-	-	-	0.2227	-	-	-	-	-

Table.16: 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
4C	1.2567	0.7957
6C	1.0703	0.9344
8C	2.1442	0.4667
10C	1.5868	0.6302
11C	0.9748	1.0259
12C	0.7027	1.4231

14C	1.164	0.8591
16C	1.486	0.6729

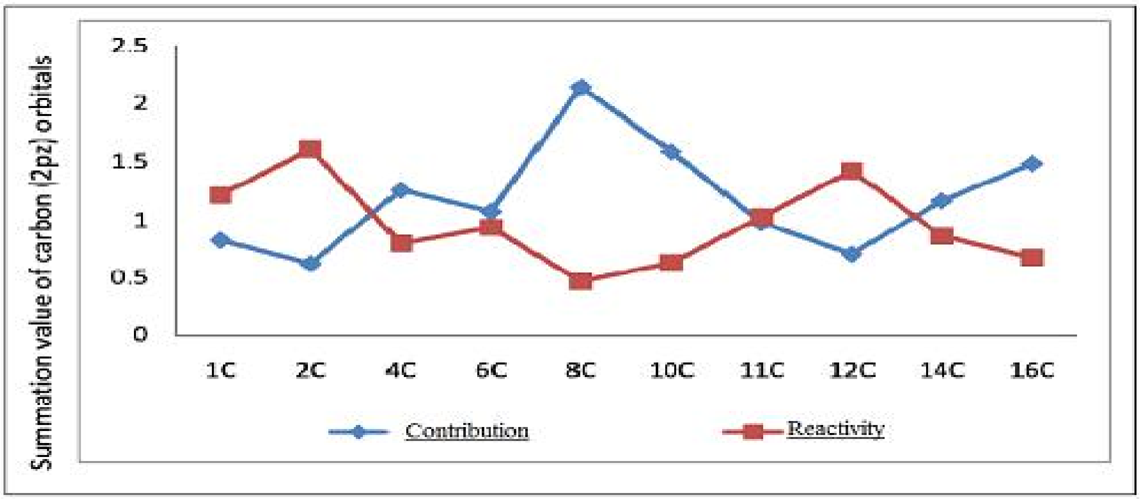

Fig.10: Sum of contributions and reactivity of atomic orbital's of, carbon in the formation of molecular orbitals of nickelocene.

The summation values shown in Table 16.And Figure 10.clearly indicates that contribution of 2pz orbital of 8C has the maximum involvement out of the ten carbon atoms in $(C_5H_5)^-$The sequence from the series are given below:
8C >10C >16C >4C >14C >6C >11C >1C >12C >2C.Eq (11)
Sum of contributions of atomic orbitals of carbon (2pz) in the formation of molecular orbitals of nickelocene is shown in Table 16.and Figure 10.where the sum of contribution of 2C of 2pzorbital's in the formation of molecular orbital's are least out of the ten carbon atoms. Hence 2C are comparatively free for complex formations. The exact order of availability of carbon atom for complex formation is given below:
2C >12C >1C >11C >6C >14C >4C >16C >10C >8C. Eq (12)
The total involvement in relation to the bonding between metal orbital derived from coefficient values are 22.6107 in ferrocene, 24.2528 in cobaltocene and 22.8486 in nickelocene hence cobaltocene is more stable than ferrocene and nickelocene. The total involvement in relation to the bonding between 2pz orbital of the ten carbon atoms of both ligands of $(C_5H_5)^-$ 19.889, 15.986 and 15.529 in ferrocene, cobaltocene and nickelocene respectively, hence ferrocene is more stable than cobaltocene and nickelocene. The total involvement of 3d, 4s and 4p orbitals of metal and 2pzorbitals of the ten carbon atoms of both ligands of $(C_5H_5)^-$ in ferrocene, cobaltocene and nickelocene respectively are 42.2528, 40.2388 and 38.3776; hence we can conclude that ferrocene is more stable than cobaltocene and nickelocene.

Population analysis
The contribution of electrons in each occupied MO is calculated by using the population analysis method introduced by Mullikan [24, 25, and26]. This method apportions the electrons of n-electron molecule in to net population $n_r$in the basis function χ(r). Let there be n_i electrons in the MO Φ_i (n_i= 0, 1, 2) and let n_{ri} symbolize the contribution of electrons in the MO Φ_i to the net population in $\chi_r$we have:

$$n_{ri} = n_i c^2_{ri} \qquad \text{Eq (13)}$$

Where, c_{ri} is the coefficient of atomic orbital for the ith MO r =1-29 in ferrocene and r=1-30 in cobaltocene and nickelocene. Eq (13) has been solved for, 58 electrons of 29 molecular orbitals in ferrocene and 59 electrons of 30 molecular orbitals in cobaltocene and nickelocene. Each MOs has two electrons in ferrocene, cobaltocene and nickelocene molecules but (the 30thMOs of cobaltocene and nickelocene have only one electron). The coefficient of atomic orbital c_{ri} is treated as Eigen vector value [24, 25, and 26].Values less than 0.1 have negligible contributions and are omitted in the calculations. Only 3dorbitals of metal and 2pzorbitals of carbon are considered in the calculation.
The summation value of population analysis of these orbitals is shown in Table 17 of ferrocene, 18 of cobaltocene and 19 of nickelocene. It is indicated that in MOs 1-17 of ferrocene, in MOs 1-19 of cobaltocene and in

MOs 1-14 of nickelocene only 2s, 2pyand 2px electrons of carbon have contributions in the formation of molecular orbital of ferrocene; cobaltocene and nickelocene hence are out of discussion.

Tables 17, 18 and 19 the result of the population analysis shows that only 2pzorbitals of carbon of (C5H5) −and 3d orbitals of metal provide electrons to MOs of ferrocene, cobaltocene and nickelocene. However, it is prominently noticeable that electrons are provided from different orbitals in the f ferrocene, cobaltocene and nickelocene, and their n_{ri} also differs

Figure11.Clearly indicates that occupied molecular orbitals of ferrocene are more electrons population contribution for the formation of molecular orbitals than cobaltocene and nickelocene molecule.

Table.17: The Sum of contribution of electrons 3d orbitals of iron and 2pz orbitals of carbon in the formation of molecular orbitals of ferrocene.

MOs	**No. of atomic orbitals**	**Eigenvector (c_{ri})**	**No. of electrons (n_i)**	**Net population (n_{ri})**
Φ18	3	0.8811	6	0.5176
Φ20	3	0.8256	6	0.4850
Φ22	3	0.8783	6	0.5161
Φ23	8	2.1169	16	1.2437
Φ24	11	2.2446	22	1.3187
Φ25	7	1.9429	14	1.1414
Φ26	8	1.9902	16	1.1692
Φ27	6	1.9034	12	1.1182
Φ28	10	2.4248	20	1.4246
Φ29	10	2.3758	20	1.3958

Summation value of population analysis, (n_{ri}) of occupied molecular orbital of ferrocene is, 10.3302.

Table.18: The Sum of contribution of electrons, 3d orbitals of cobalt and, 2pzorbitals of carbon in the formation of molecular orbitals of cobaltocene.

MOs	**No. of atomic orbitals**	**Eigenvector (c_{ri})**	**No. of electrons (n_i)**	**Net population (n_{ri})**
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_{ri}) of occupied molecular orbital of cobaltocene is 10.0715.

Table.19: The Sum of contribution of electrons, 3d orbitals of nickel and, 2pzorbitals of carbon in the formation of molecular orbitals of nickelocene.

MOs	No. of atomic orbitals	Eigenvector (c_{ri})	No. of electrons (n_i)	Net population (n_{ri})
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

Sum of Summation value of population analysis, (n_{ri}) of occupied molecular orbital of nickelocene is, 10.0609.

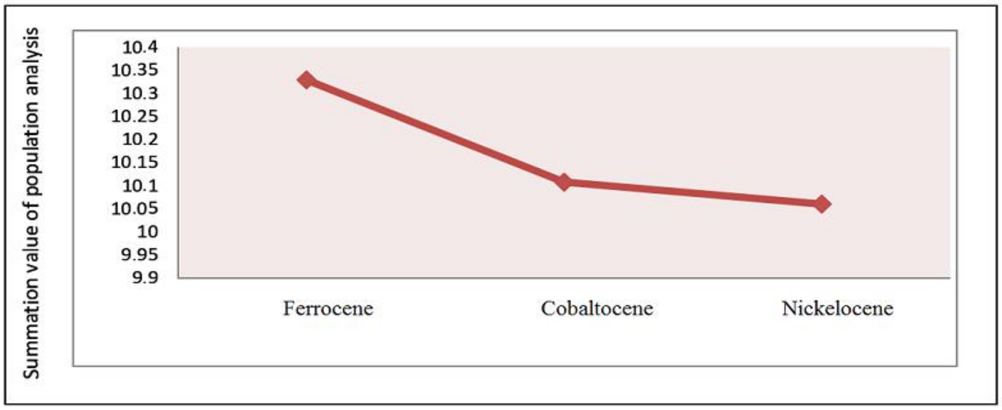

Fig.11: Comparison Summation value of population analysis of occupied molecular orbital of ferrocene, cobaltocene and nickelocene molecules in 3d orbital of metal and 2pz orbitals of carbon.

IV. CONCLUSION

We studied the electronic structure and geometry optimization of ferrocene, 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 -2.03849 to -0.54008eV in ferrocene -0.86738 to -0.56256 eV in cobaltocene and -9.90743 to -0.64271 eV in nickelocene)) formed between 3d orbitals and 2pz orbitals are the most stable molecular orbitals. The less stable orbitals are in the energy ranges of -0.53616 to -0.10707 eV in ferrocene,-0.37685 to -0.03634 eV in cobaltocene and -0.56142 to -0.10622 eV nickelocene. Eigenvectors of ferrocene, cobaltocene and nickelocene show that the first 13 MOs in ferrocene 12 MOs cobaltocene and 14 MOs nickelocene are formed by various 3d orbitals of metal and 2pz orbital of carbon of (C_5H_5)-and the most stable MOs. The next 9 MOs in ferrocene, 12 MOs of cobaltocene and 11 MOs of nickelocene are formed by the interaction of 4s and 4p orbitals of metal and2pz orbital of carbon of $(C_5H_5)^-$and these MOs are comparatively less stable orbitals. Out of the 3d orbitals of ferrocene , cobaltocene and nickelocene molecules the 3dyz orbitals have maximum involvement in the formation of molecular orbitals, whereas the 4pz orbital out of 4s and 4p orbital of iron , 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 of4pz >4py >4s >4pxand 3dyz >$3dx^2{-}y^2$>$3dz^2$>3dxz in ferrocene, 4s >4pz >4py >4pxand 3dyz >3dxy >3xz >3dz^2 >3dx^2−y^2 in cobaltocene and 4py >4px >4s >4pz and 3dyz >3dx^2−y2 >3dxy >3dxz >3dz^2 in nickelocene. The total involvement in relation to the bonding between metal orbital derived from coefficient values are 22.6107 in ferrocene , 24.2528 in cobaltocene and 22.8486 in nickelocene hence cobaltocene is more stable than ferrocene and nickelocene molecules. The total involvement in relation to the bonding between 2pzorbital of the ten carbon atoms of both ligands of $(C_5H_5)^-$19.889, 15.986 and 15.529 in ferrocene, cobaltocene and nickelocene respectively, hence ferrocene is more stable than cobaltocene and 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 $(C_5H_5)^-$in ferrocene , cobaltocene and nickelocene respectively are 42.2528 , 40.2388 and 38.3776 hence we can conclude that ferrocene is more stable than cobaltocene and nickelocene molecules. The population analysis shows that only 2pz orbitals of carbon of $(C_5H_5)^-$and 3d orbitals of metal provide electrons to MOs of ferrocene, cobaltocene and nickelocene molecules.We recommend to simulate bigger molecules using higher basis sets and to study more properties of the molecules. Larger basis sets provide approximations more accurately by imposing fewer restrictions on the interaction of electrons in space.

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