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## Density Functional Study of Molecular Orbitals of Cobaltocene and Nickelocene Molecules

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### 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 (C<sub>5</sub>H<sub>5</sub>)<sup>-</sup> 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>3dxy>3dxz>3d<sub>z</sub><sup>2</sup>>3d<sub>x</sub><sup>2</sup>-y<sub>2</sub>. 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>3d<sub>x</sub><sup>2</sup>-y<sub>2</sub>>3dxy>3dxz>3d<sub>z</sub><sup>2</sup> molecules. The total involvement of 3d, 4s and 4p orbitals of metal and 2pz orbitals of the ten carbon atoms of both ligands of (C<sub>5</sub>H<sub>5</sub>)<sup>-</sup> 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 (C<sub>5</sub>H<sub>5</sub>)<sup>-</sup> 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

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### 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

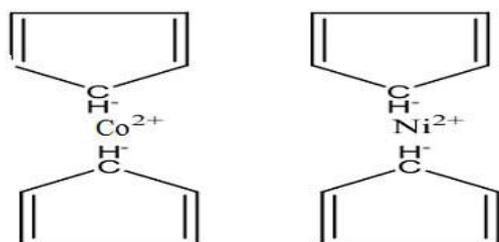
1. combination of Beck's three-parameter exchange functional and Lee-Yang-Parr correlation functional with 6-31G
2. basis set.

These methods are found in Gaussian 03W program. B3LYP is a DFT method with hybrid functional that provides qualitative results at a lower cost than abinitio methods with a comparable 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].

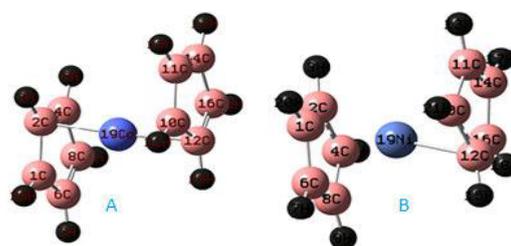
## Results and Discussion

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 Å, and nickelocene 1.392-1.98 Å 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

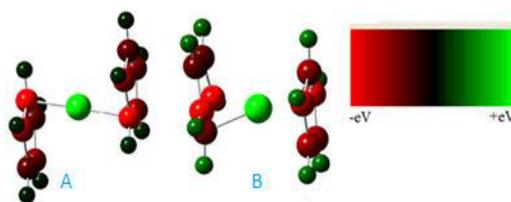
stable metabolically. As shown in **Figure 2A and Table 1** the bond connectivity of Co-(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> of the two ligands are asymmetrical. The optimized bond length of cobalt atom with the two carbon atoms has fewer variations. The cobalt atom in cobaltocene is bonded with C2 atom of bond length 1.969 (°Å) in one side of the ligand and with C12 of bond length 1.994 (°Å) 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°Å. As shown in **Figure 2B and Table 2**. The bond connectivity of Ni-(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> of the two ligands are asymmetrical. The nickel atom in nickelocene is bonded with C12 atom of bond length 1.976 (°Å) 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 -67.377° 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°Å. 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



**Figure 1** Structure of cobaltocene and nickelocene molecules.



**Figure 2** The optimized structures of cobaltocene and nickelocene molecules.



**Figure 3** The Millikan charge distributions of cobaltocene and nickelocene Molecules.

**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 (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	109.56	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.

Entry	Bond length(°Å)	Entry	Bond angle (o)	Entry	Dihedral angle (o)
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	1.976				

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 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 -0.56142 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.

**Table 3** Important parametric properties of the molecules calculated at the DFT/B3LYP levels in 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 (ηin eV)	0.04129	0.04065
Global softness (S in eV)	24.216	24.603
Electro negativity (χin eV)	0.6039	0.6021
Chemical potential (μin eV)	-0.6039	-0.6021
Dipole moment (μin Debye)	1.695	1.931
Mulliken charge distributions (M.C.D in e)	± 1.13	± 1.692

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

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 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. The above figures show 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 AOs of two ( $C_5H_5$ )- and nine orbital of cobalt and nickel. These fifty-nine AOs  $\chi_1$  to  $\chi_{59}$  on LCAO approximation form same number of MOs,  $\Phi_1$  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, 3dx<sup>2</sup>-y<sup>2</sup>, 3dz<sup>2</sup>, 3dxy, 3dxz, 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 involved in the formation of  $\sigma$  bond between C-C and C-H. The orbitals involved in  $\sigma$  bond hence shall remain out of discussion. The 2pz orbitals of ten carbons and nine orbitals of cobalt or nickel i.e. in total nineteen orbitals are relevant to our discussion in respect of bonding between cobalt or nickel orbitals and 2pz orbital of ( $C_5H_5$ )-. These atomic orbitals are  $\chi_4$ ,  $\chi_8$ ,  $\chi_{12}$ ,  $\chi_{16}$ ,  $\chi_{20}$ ,  $\chi_{24}$ ,  $\chi_{28}$ ,  $\chi_{32}$ ,  $\chi_{36}$  and  $\chi_{40}$  of carbon and  $\chi_{41}$  to  $\chi_{49}$  of cobalt and nickel. The coefficients of these orbitals are the eigenvector values of  $\chi$  [21]. They express the forms of MOs i.e. the extent of involvement of  $\chi$  in the formation of  $\Phi$ . 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 in **Tables 4-11** respectively. The coefficients of these orbital are the Eigen vector

values of,  $\chi$  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  $\chi$  in the formation of  $\Phi$ . The calculated Eigen vector values of atomic orbitals of Co and Ni in the formation of molecular orbitals in cobaltocene and nickelocene in **Tables 4, 5, 8, 9** respectively and the calculated Eigen vector values of 2pz orbital of carbon are given in **Tables 6, 7, 10, 11**. **Tables 5, 7, 9, 11** are summation of Eigen vector values of cobaltocene and nickelocene. Negative, Zero and near zero coefficient values are negligible contributions [21,23] of electrons and have been excluded from the **Tables (Figure 4)**.

Out of 59 molecular orbital Eigen values of cobaltocene we shall discuss only 24 of them described in **Table 4**, for cobalt orbitals and **Table 6**, for carbon orbitals. The first 12MOs are  $\Phi_{20}$  - $\Phi_{31}$  formed 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 are  $\Phi_{36}$ - $\Phi_{38}$ ,  $\Phi_{41}$ - $\Phi_{42}$ ,  $\Phi_{46}$ - $\Phi_{47}$ ,  $\Phi_{50}$ - $\Phi_{51}$ ;  $\Phi_{54}$ - $\Phi_{55}$  and  $\Phi_{56}$  have contributions from vacant 4s, 4px, 4py and 4pz orbital of cobalt and 2pz orbital of carbon. These MOs with energies between -0.37685 to -0.03634 eV are comparatively less stable. To examine the extent of involvement of 3d, 4s, and, 4p orbital 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 5**.

The summation values given 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:

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

3dyz>3dxy>3dxz>3dz<sup>2</sup>>3dx<sup>2</sup>-y<sup>2</sup> 1

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<sup>2</sup>-y<sup>2</sup> 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<sup>2</sup>-y<sup>2</sup> 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:

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

3dx<sup>2</sup>-y<sup>2</sup>>3dz<sup>2</sup>>3dxz>3dxy>3dyz 2

The summation values shown in **Table 7** and **Figure 6**, clearly indicates that contribution of 2pz orbital of <sup>6</sup>C has the maximum involvement out of the ten carbon atoms in ( $C_5H_5$ )-. The sequence from the series are given below:

<sup>6</sup>C><sup>10</sup>C><sup>1</sup>C><sup>16</sup>C><sup>8</sup>C><sup>12</sup>C><sup>2</sup>C><sup>11</sup>C><sup>4</sup>C><sup>14</sup>C 3

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<sub>c</sub> of 2pz orbital's in the formation of molecular orbital's are least out of the ten carbon atoms. Hence <sup>14</sup>C are comparatively free for

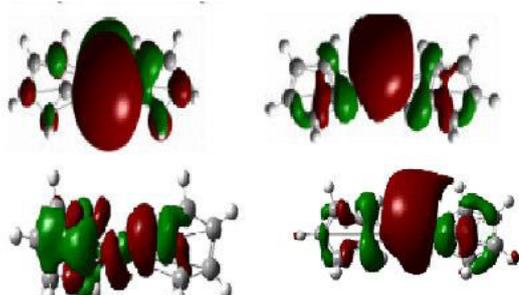
**Table 4** Contributions of orbitals of cobalt and their summation values in the formation of molecular orbitals of cobaltocene.

MOs	4s	4px	4py	4pz	3dx <sup>2</sup> -y <sup>2</sup>	3dz <sup>2</sup>	3dxy	3dxz	3dyz
	$\chi_{41}$	$\chi_{42}$	$\chi_{43}$	$\chi_{44}$	$\chi_{45}$	$\chi_{46}$	$\chi_{47}$	$\chi_{48}$	$\chi_{49}$
$\Phi_{20}$	-	-	-	-	-	-	-	-	0.2124
$\Phi_{21}$	-	-	-	-	-	-	-	0.2335	0.3224
$\Phi_{22}$	-	-	-	-	-	-	0.2113	-	-
$\Phi_{23}$	-	-	-	-	0.2507	0.4737	0.2664	0.2327	0.1436
$\Phi_{24}$	-	-	-	-	0.5537	0.1378	0.4186	0.1448	0.2731
$\Phi_{25}$	0.1198	-	-	-	-	0.5281	-	0.3033	0.5717
$\Phi_{26}$	-	-	-	-	0.2652	0.1081	0.5281	0.3717	0.3035
$\Phi_{27}$	-	-	-	-	0.1445	-	0.2931	0.2063	-
$\Phi_{28}$	-	-	-	-	0.1103	0.1402	0.2339	-	0.2297
$\Phi_{29}$	-	-	-	-	-	0.2052	0.2116	0.1243	-
$\Phi_{30}$	-	-	-	-	-	0.5131	0.2416	0.3996	0.1363
$\Phi_{31}$	-	-	-	-	0.3741	-	-	0.3523	0.4225
$\Phi_{36}$	0.3346	0.9288	-	0.407	-	-	-	-	-
$\Phi_{37}$	0.3259	-	0.8777	0.565	-	-	-	-	-
$\Phi_{38}$	0.6188	-	-	0.2691	-	-	-	-	-
$\Phi_{41}$	0.3195	-	0.3626	0.4823	-	-	-	-	-
$\Phi_{42}$	0.3148	-	0.3549	0.3479	-	-	-	-	-
$\Phi_{46}$	0.2767	0.3026	-	0.3002	-	-	-	-	-
$\Phi_{47}$	0.3329	-	0.2698	0.2911	-	-	-	-	-
$\Phi_{50}$	0.7259	-	0.2913	0.3794	-	-	-	-	-
$\Phi_{51}$	0.5741	0.5317	0.3413	0.7871	-	-	-	-	-
$\Phi_{54}$	-	0.238	0.2945	0.2227	-	-	-	-	-
$\Phi_{55}$	0.3738	0.2889	0.3878	-	-	-	-	-	-
$\Phi_{56}$	0.2297	-	-	-	-	-	-	2.3685	-

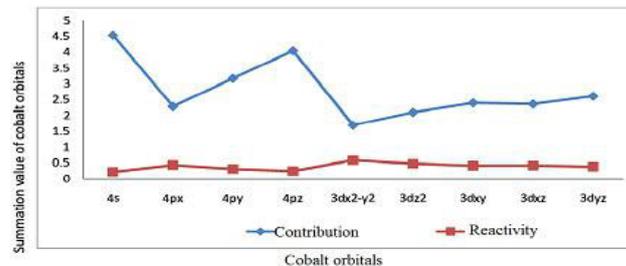
N.B: orbitals having coefficient values above 0.10 have only been considered.

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

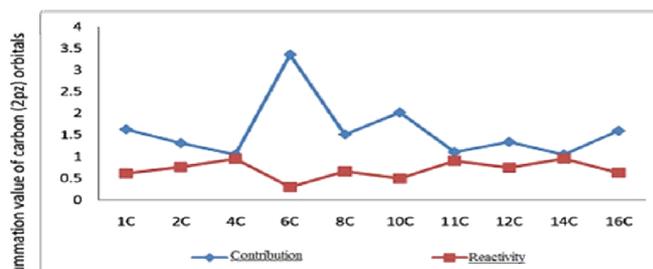
Atomic orbital's of Co	Sum of contributions of orbital's of Co	Sum of reactivity
4s	4.5465	0.2199
4p <sub>x</sub>	2.29	0.4367
4p <sub>y</sub>	3.1799	0.3145
4p <sub>z</sub>	4.0518	0.2468
3dx <sup>2</sup> -y <sup>2</sup>	1.6985	0.58875
3dz <sup>2</sup>	2.1062	0.4748
3d <sub>xy</sub>	2.4046	0.4159
3d <sub>xz</sub>	2.3685	0.4222
3d <sub>yz</sub>	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:

**Table 6** Contributions of 2pz orbitals of carbon atoms in (C<sub>5</sub>H<sub>5</sub><sup>-</sup>) in the formation of molecular orbitals of cobaltocene.

MOs	1C	2C	4C	6C	8C	10C	11C	12C	14C	16C
	χ <sup>4</sup>	χ <sup>8</sup>	χ <sup>12</sup>	χ <sup>16</sup>	χ <sup>20</sup>	χ <sup>24</sup>	χ <sup>28</sup>	χ <sup>32</sup>	χ <sup>36</sup>	χ <sup>40</sup>
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	-	0.238	-	-	-	-	-	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	-	-	-	-	-	-	-	-	-	-
S	1.6332	1.3124	1.0519	3.3601	1.5142	2.0235	1.1071	1.3382	1.0473	1.5984

**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

$${}^{14}\text{C} > {}^4\text{C} > {}^{11}\text{C} > {}^2\text{C} > {}^{12}\text{C} > {}^8\text{C} > {}^{16}\text{C} > {}^1\text{C} > {}^{10}\text{C} > {}^6\text{C}$$

4

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<sub>5</sub>H<sub>5</sub><sup>-</sup>). 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<sub>5</sub>H<sub>5</sub><sup>-</sup>). 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<sub>5</sub>H<sub>5</sub><sup>-</sup>). 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:

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

$$3dyz > 3dx^2 - y^2 > 3dxy > 3dxz > 3d^2z \quad 5$$

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<sup>2</sup>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<sup>2</sup>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:

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

$$3dyz > 3dxz > 3dxy > 3dx^2 - y^2 > 3dyz \quad 6$$

The summation values shown in **Table 11** and **Figure 8** clearly indicates that contribution of 2pz orbital of <sup>8</sup>C has the maximum involvement out of the ten carbon atoms in (C<sub>5</sub>H<sub>5</sub><sup>-</sup>). The sequence from the series are given below:

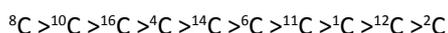
**Table 8** Contributions of orbitals of nickel in the formation of molecular orbitals of nickelocene.

MOs	4s	4p x	4py	4pz	3dx <sup>2</sup> -y <sup>2</sup>	3dz <sup>2</sup>	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	-	-	-	-	-
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.

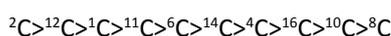
**Table 9** Sum of contributions and reactivity of atomic orbital's of nickel in the formation of molecular orbitals of nickelocene.

Atomic orbital's of Ni	Sum of contributions of orbital's of Ni	Sum of reactivity
4s	2.4466	0.4087
4p <sub>x</sub>	4.277	0.2338
4p <sub>y</sub>	4.3833	0.2281
4p <sub>z</sub>	1.9529	0.5121
3dx <sup>2</sup> -y <sup>2</sup>	1.9439	0.5144
3d <sub>z</sub> <sup>2</sup>	1.5768	0.6342
3d <sub>xy</sub>	1.9095	0.5237
3d <sub>xz</sub>	1.7671	0.5657
3d <sub>yz</sub>	2.2815	0.4383

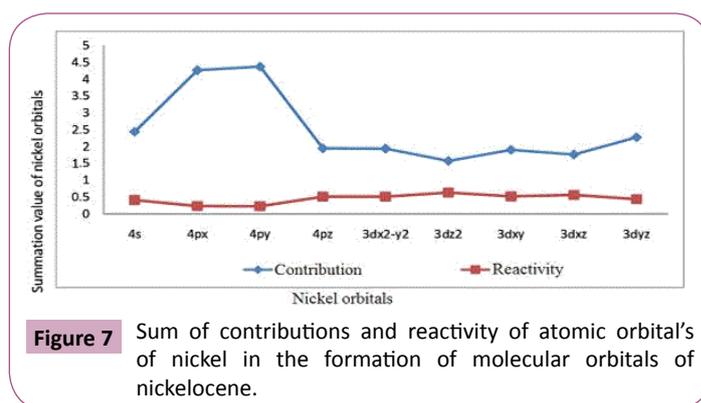


7

Sum of contributions of atomic orbitals of carbon (2p<sub>z</sub>) in the formation of molecular orbitals of nickelocene is shown in **Table 11 and Figure 8** where the sum of contribution of <sup>2</sup>C of 2p<sub>z</sub> orbital's in the formation of molecular orbital's are least out of the ten carbon atoms. Hence <sup>2</sup>C are comparatively free for complex formations. The exact order of availability of carbon atom for complex formation is given below:



8

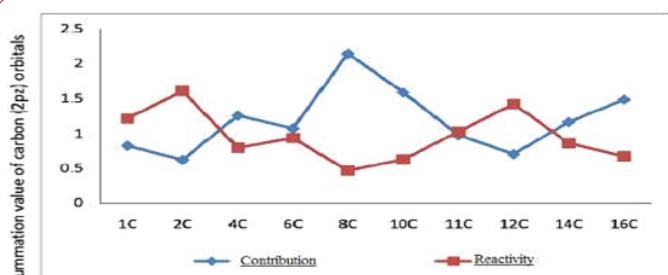
**Figure 7** Sum of contributions and reactivity of atomic orbital's of nickel in the formation of molecular orbitals of nickelocene.

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. The total involvement in relation to the bonding between 2p<sub>z</sub> orbital of the ten carbon atoms of both ligands of (C<sub>5</sub>H<sub>5</sub>)<sup>-</sup>: 15.986 and 15.529 in cobaltocene and nickelocene respectively, hence cobaltocene is more stable than nickelocene. The total involvement of 3d, 4s and 4p orbitals of metal and 2p<sub>z</sub> orbitals of the ten carbon atoms of both ligands of (C<sub>5</sub>H<sub>5</sub>)<sup>-</sup> in cobaltocene and nickelocene respectively are 40.2388, and 38.3776 hence we can conclude that cobaltocene is more stable than nickelocene.

**Table 10** Contributions of 2pz orbitals of carbon atoms in (C<sub>5</sub>H<sub>5</sub>)<sup>-</sup> in the formation of molecular orbitals of nickelocene.

MOs	1C	2C	4C	6C	8C	10C	11C	12C	14C	16C
	$\chi^4$	$\chi^8$	$\chi^{12}$	$\chi^{16}$	$\chi^{20}$	$\chi^{24}$	$\chi^{28}$	$\chi^{32}$	$\chi^{36}$	$\chi^{40}$
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	-	-	-	-	-
S	0.8235	0.6212	1.2567	1.0703	2.1442	1.5868	0.9748	0.7027	1.164	1.486

N.B: orbital having coefficient value above, 0.10 have only been considered.



**Figure 8** Sum of contributions and reactivity of atomic orbital's of, Ni in the formation of molecular orbitals of nickelocene.

### Population Analysis

The contribution of electrons in each occupied MO is calculated by using the population analysis method introduced by Mullikan [24-26]. This method apportions the electrons of  $n$ -electron molecule in to net population  $n_r$  in the basis function  $\chi(r)$ . Let there be  $n_i$  electrons in the MO  $\Phi_i$  ( $n_i=0, 1, 2$ ) and let  $n_{ri}$  symbolize the contribution of electrons in the MO  $\Phi_i$  to the net population in  $\chi$ , we have:

$$n_r = \sum_i n_i c_{ri} \quad (9)$$

Where,  $c_{ri}$  is the coefficient of atomic orbital for the  $i$ th MO  $r=1-30$  in cobaltocene and nickelocene. Eq (9) has been solved

for, 60 electrons of 30 molecular orbitals in cobaltocene and nickelocene. Each MOs has two electrons in cobaltocene and nickelocene but (the 30<sup>th</sup> MOs of cobaltocene and nickelocene have only one electron). The coefficient of atomic orbital  $c_{ri}$  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 (C<sub>5</sub>H<sub>5</sub>)<sup>-</sup> 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

**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	
<sup>1</sup> C		0.8235			1.2143	
<sup>2</sup> C		0.6212			1.6098	
<sup>4</sup> C		1.2567			0.7957	
<sup>6</sup> C		1.0703			0.9344	
<sup>8</sup> C		2.1442			0.4667	
<sup>10</sup> C		1.5868			0.6302	
<sup>11</sup> C		0.9748			1.0259	
<sup>12</sup> C		0.7027			1.4231	
<sup>14</sup> C		1.164			0.8591	
<sup>16</sup> C		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 ( $c_{ij}$ )	No. of electrons ( $n_i$ )	Net population ( $n_{ij}$ )
$\Phi 20$	2	0.5855	4	0.3344
$\Phi 21$	3	0.8773	6	0.5154
$\Phi 22$	2	0.5907	4	0.3470
$\Phi 23$	10	2.1549	20	1.2661
$\Phi 24$	8	1.8713	16	1.0994
$\Phi 25$	6	1.8031	12	1.0593
$\Phi 26$	8	2.6812	16	1.3475
$\Phi 27$	10	2.2936	20	1.1527
$\Phi 28$	11	2.3559	22	1.1829
$\Phi 29$	9	1.6489	18	0.8279
$\Phi 30$	12	2.9759	12	0.9391

Summation value of population analysis, ( $n_{ij}$ ) 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 ( $c_{ij}$ )	No. of electrons ( $n_i$ )	Net population ( $n_{ij}$ )
$\Phi 15$	3	0.8252	6	0.4884
$\Phi 16$	2	0.4285	4	0.2537
$\Phi 18$	1	0.3605	2	0.2134
$\Phi 19$	1	0.4718	2	0.2793
$\Phi 20$	1	0.5297	2	0.4163
$\Phi 21$	3	0.7034	6	0.5529
$\Phi 23$	4	1.1606	8	0.9122
$\Phi 24$	6	1.5789	12	1.2410
$\Phi 25$	5	1.7438	10	1.0979
$\Phi 26$	2	1.2357	4	0.7780
$\Phi 27$	4	0.9055	8	0.5701
$\Phi 28$	7	1.9303	14	1.1425
$\Phi 29$	8	2.2311	16	1.3206
$\Phi 30$	12	1.3426	24	0.7947

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

nickelocene) formed between 3d orbitals and 2pz orbitals are the most stable molecular orbitals. The less stable orbitals are in the energy ranges of -0.37685 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 nickelocene are formed by various 3d orbitals of metal and 2pz orbital of carbon of ( $C_5H_5$ )<sup>-</sup> 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 ( $C_5H_5$ )<sup>-</sup> and these MOs are comparatively less stable orbitals.

Out of the 3d orbitals of cobaltocene and nickelocene molecules the 3dyz 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<sup>2</sup>>3dx<sup>2</sup>-y<sup>2</sup> in cobaltocene, and 4py>4px>4s>4pz and 3dyz>3dx<sup>2</sup>-y<sup>2</sup>>3dxy>3dxz>3dz<sup>2</sup> 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. The total involvement in relation to the bonding between 2pz orbital of the ten carbon atoms of both ligands of  $(C_5H_5)^-$  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  $(C_5H_5)^-$  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  $(C_5H_5)^-$  and 3d orbitals of metal provide electrons to MOs of cobaltocene and nickelocene.

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