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Molecular and Electronic Structure of Chromium (III) Cyclopentadienyl Complexes

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***Abstract*—**Here, we have shown the reaction of $[Cr(ArN(CH_2)_3NAr)_2Cl_2]$ (1) where (Ar = 2,6-$Pr^i{}_2C_6H_3$) and in presence of NaCp (2) (Cp= C_5H_5 = cyclopentadien), with a center coordination η^5 interaction between Cp as co-ligand and chromium metal center, for optimization we used density functional theory (DFT), under methods, explicitly including electrons correlations, for the final calculations as MB3LYP (Becke) (Lee–Yang–Parr) level of theory we used to obtain more exact results. This complex was calculated as electronic energy for molecular system, because the calculation accounting all electrons correlations interactions. The optimised of $[Cr(ArN(CH_2)_3NAr)_2(\eta^5\text{-}Cp)]$ (Ar = 2,6-$Pr^i{}_2C_6H_3$ and Cp = C_5H_5) was found to be thermally stable. By using Dewar-Chatt-Duncanson model, as a basis of the molecular orbital (MO) analysis and showed the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital LUMO.

***Keywords*—**Chromium (III) cyclopentadienyl complexes, DFT, MO, HOMO, LUMO.

I. Introduction

THE Chromium complexes have played a special role in the history of olefin polymerization [1]-[3] and also dimmer of chromium complexes has been investigated, also synthetic computational investigations by Power et al and other groups, those were followed at low-valent metals (i.e., with d^5 and d^6 configuration). [4], [5]

To date, most of the Group 4 and Group 5 catalysts for polymerisation have been supported by one or more cyclopentadienyl rings, [6]-[11] but there is a growing interest in the use of new anciliary, non cyclopentadienyl ligands, such as chelating diamides or diamido donor ligands. [12], [13] Yi. The syntheses of Chromium dioxo with Imido via treatment of $[Cr(\mu\text{-}Cl)(Nacnac)]_2$(Nacnac = $HC(C(Me)NC_6H_3\text{-}^iPr_2)_2$) in ration 2.5 equiv of KC_8 in toluene to isolation of an inverted-sandwich toluene bridged complex ($\mu\text{-}\eta^6.\eta^6\text{-}C_7H_8$)$[Cr(Nacnac)]_2$, then this complex was reacted with benzene, $MesN_3$ Mes= 2,4,6-$C_6H_2Me_3$) and Ph_2N_2 to obtained monomeric $Cr(O)_2$(Nacnac) with 8 electron reductant, $[Cr(NMes)_2(Nacnac)]$ and $(\mu\text{-}NPh)(Nacnac)]_2$ respectively. [12]

Again the synthesis and reactivity of chromium(III) cyclopentadienyl β-diketiminato compounds starting from $[Cr\{CH(ArNCMe)_2\}Cl(\mu\text{-}Cl)\}]_2$ and $[Cr\{CH(ArNCMe)_2\}(\mu\text{-}Cl)\}]_2$ (Ar = 2,6-$Pri_2C_6H_3$) was achieved by Smith et al. following activation of $[Cr\{CH(ArNCMe)_2\}(\mu\text{-}Cl)\}]_2$ by MeI. On the other hand, Cr(III) halide species were synthesized by oxidation of the Cr(II) complexes with lead(II) halides.[13]

The Schrödinger Equation mainly detailing wave function theory as method of determining electronic structure was published by Schrödinger and all information for a system is contained in a wave function. Also time-independent was developed by Schrödinger Equation [14]-[17] can be solved and gives the energy of the system.

Density functional theory (DFT), discussed in detail in the following sections, is based on the use of electron density as an alternative to wave functions. There are significant advantages to a computational theory based on electron densities. The first is in relation to computational efficiency; the electron density depends on three spatial coordinates in contrast to the 4N coordinates that wave function theory depends on (three spatial and one spin per electron). Therefore, large systems can theoretically be modelled. In addition, electron correlation is conceptually easier to include in DFT.

Using both theoretical methods and experimental techniques has highly interest for many years to form determination of the structural and spectroscopic properties of compounds.

On the past ten years, the computational methods calculating the electronic structure of molecular systems such DFT was found the favorite one, and the information can be Obtained from this methods such molecule geometry, vibrational frequencies, atomic charges, dipole moment, and others and this is because of its great accuracy in reproducing the experimental values [15], [16].

The computational and theoretical studies by using Density Functional Theory (DFT) method has increased as this method helps to determine the molecular data such bond lengths and bond angles and molecular orbital analysis. The use of advanced calculation by applying the Beck's three parameters, Lee, Yang and Parr (B3LYP) approximation into the DFT method has improved the data accuracy. [17]

Recently a whole issue of chemical reviews dedicated to computational transition metal chemistry showed how the introduction of DFT has revolutionized this field.

II. Method

A complex of $[Cr(ArN(CH_2)_3NAr)_2(\eta^5\text{-}Cp)]$ where (Ar = 2,6-$Pr^i{}_2C_6H_3$ and Cp= C_5H_5) (**3**) as mono-complex, can be make via the reaction of $[Cr(ArN(CH_2)_3NAr)_2Cl_2]$ (**1**) where (Ar = 2,6-$Pr^i{}_2C_6H_3$ and Cp= C_5H_5) (**2**) in presence of NaCp at Fig. 1

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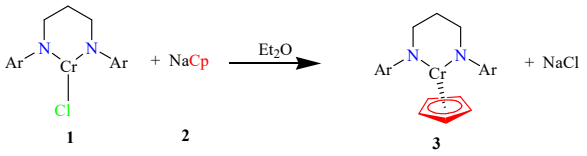

(Ar = 2,6-$Pr^i_2C_6H_3$)

Fig. 1 Preparation of $[Cr(ArN(CH_2)_3NAr)_2Cl(\eta^5\text{-}Cp)]$ (Ar = 2,6-$Pr^i_2C_6H_3$ and Cp= C_5H_5)

III. Result and Discussion

Recently a whole issue of Chemical Reviews dedicated to computational transition metal chemistry showed how the introduction of DFT has revolutionized this field.

Our spin-unrestricted carried out under BP86/TZVP calculations on the staggered and eclipsed model of $[Cr(ArN(CH_2)_3NAr)_2(\eta^5\text{-}Cp)]$ (Ar = 2,6-$Pr^i_2C_6H_3$ and Cp= C_5H_5) is in agreement with the DFT calculations.

The DFT structure confirmed the constitution of **3**, which is shows CS symmetry. There is a mirror plane that divides the N(1), C(26) and N(2),C(1) ligand through the chromium centre (C(27)-Cr-Cp). The nitrogen donors chelate around the chromium centre as expected, and the metal centre resides in a distorted tetrahedral environment defined by N, N' and Cp (Fig. 2).

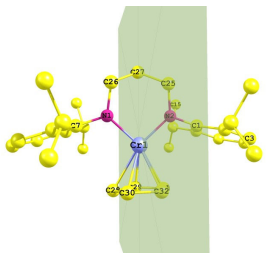

Fig. 2 Cs Symmetry of **3** via chemcraft from point group selection

The spin density and bond energy under Cs point group of the complex $[Cr(ArN(CH_2)_3NAr)_2(\eta^5\text{-}Cp)]$ was shown in Table I.

TABLE I
Selected Some Parameters of Spin Density and Bond Energy

Complex	$[Cr(ArN(CH_2)_3NAr)_2(\eta^5\text{-}Cp)]$ (Ar = 2,6-$Pr^i_2C_6H_3$ and Cp= C_5H_5)
	ADF
spin density	1.2988
Bond Energy	-17.28746945 a.u.
Bond Energy	-470.41597865 eV
Bond Energy	-10848.05kcal/mol
point group	Cs-Sym

The chelate bite angle, defined by the N(1)-Cr-N(2) bond angle of 97.004° derives from the short three-carbon bridge. The N(2)-Cr-Cp bond angle is 108.546°, N(1)-Cr-Cp, N(2)-Cr-N(1), Cr-N(2)-C(1) and Cr-N(1)-C(7) bonds angles are 102.007°, 95.840°, 119.971 and 119.971 respectively.

The structure of **3** is shown in Fig. 3.

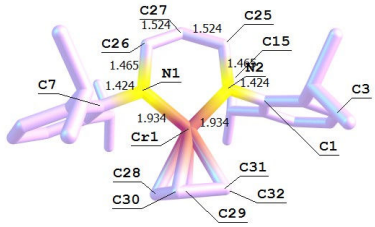

Fig. 3 Molecular structure of 3 via chemcraft Sticks

The intramolecular N- bonds showed the coordination sphere around the metal centre in case of six-membered ring as shown (Fig. 4.)

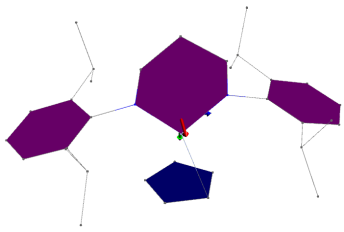

Fig. 4 Molecular structure of 3 via Avogadro program

The inclusion of the three methylene bridge unit in **3** substantially opens the coordination sphere around the metal centre, as reflected by the greater flexibility of chelate bite angles, is 348.478° around the metal centre < N(1)-Cr-N(2) as compared to the perversely work [18], has been shown in Table II.

Again supporting information of the frontier orbitals of HOMO and LUMO of the complex $Cr(ArN(CH_2)_3NAr)_2(\eta^5\text{-}Cp)]$ (Ar = 2,6-$Pr^i_2C_6H_3$ and Cp= C_5H_5), via the Dewar-Chatt-Duncanson model [19], as a basis of the molecular orbital (MO) analysis was showed the correlation between the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital LUMO is shown in Fig. 5.

TABLE II
Selected Bond Lengths and Angles in **3**

Bond	Length (/Å)	Fragment	Angle (/o)
Cr-N(1)	1.934	N(2)-Cr-N(1)	95.840
Cr-N(2)	1.934	Cr-N(2)-C(1)	119.971
Cr-Cp	2.0323	N(1)-Cr-Cp	126.319
N(1)-C(26)	1.465	N(2)-Cr-Cp	126.319
N(2)-C(25)	1.465	Cr-N(1)-C(7)	119.971
N(1)-C(7)	1.424		
N(2)-C(1)	1.424		

The highest occupied molecular orbital (HOMO) energy, the lowest unoccupied molecular orbital (LUMO) and the energy gap of HOMO and LUMO for compound **3** has been shown in Fig. 6.

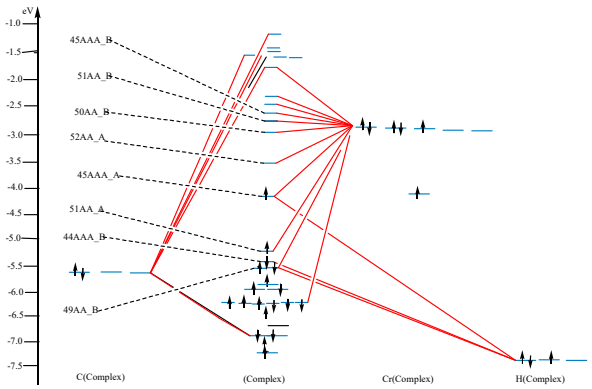

Fig. 5 Frontier orbitals of HOMO and LUMO of **3**

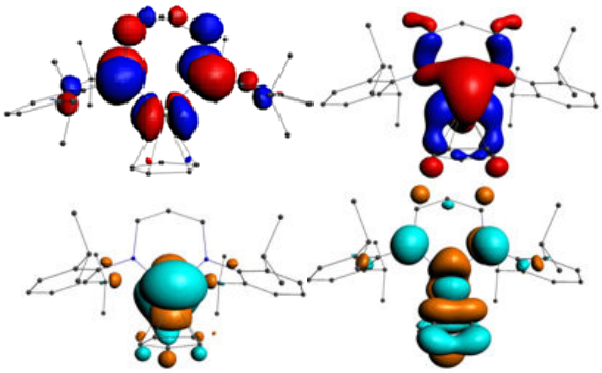

Fig. 6 HOMO and LUMO of orbitals α and β

The most common of analysis method is Mulliken population, because it is one of simplest method. [20] The main key component is the matrix composed of the elements $D_{\alpha\beta}$, the diagonal elements $D_{\alpha\alpha}$ give the interaction of an AO_α with itself (summed over all MOs). The overlap population of one AO with another can be via off-diagonal elements. [21] The half the overlap population in the Mulliken analysis is assigned to each contributing orbital, giving the total population of each AO, the gross atomic population can be optioned via the summing over all the atomic orbitals on a specific atom. [22], [23]

The AO of Chromium (III) cyclopentadienyl complexes calculated are given in Table III. From the point that chromium (III) has a configuration $[Ar]_{18}$ $3d^3$, this is should only be 3e at the 3d atomic orbitals, but there is obviously more than 3e in the outer orbital of metal center table 3. This extra population comes from the carbon and nitrogen atoms which should each have 4e and 5e, respectively; this is in fact show a depletion of electron density. Summing all the populations for all the orbitals on a single atom as first step, then subtracting the nuclear charge gives the partial charge on each atom. In the complex of Chromium (III) cyclopentadienyl the charges are 0.8928 for chromium and -0.7673 for each nitrogen atoms. Thus, overall the more electron-rich nitrogen atom can donated electrons density to from coordination bond to the less electron-rich chromium center atom leaving them with sigma and coordination bonds. Others charges of atoms are given in Table III.

TABLE III
SELECTED PARAMETERS OF SOME ATOMS ARE IN COMPLEX OF **3**

Atom	Charge	Spin density		S	P	D
N	-0.7673	-0.0388	A:	0.9079	1.923	0.0333
			B:	0.9204	1.9554	0.0272
N	-0.7673	-0.0388	A:	0.9079	1.923	0.0333
			B:	0.9204	1.9554	0.0272
Cr	0.8928	3.1685	A:	0.2033	0.2057	3.7289
			B:	0.0736	0.089	0.8068
C	-0.0802	0.0023	A:	0.7116	1.2963	0.0334
			B:	0.7105	1.2955	0.033
C	-0.1017	-0.0524	A:	0.7125	1.2774	0.0348
			B:	0.716	1.3282	0.0329
C	-0.1011	-0.0358	A:	0.7135	1.2848	0.0343
			B:	0.7157	1.3199	0.0329
C	-0.0802	0.0023	A:	0.7116	1.2963	0.0334
			B:	0.7105	1.2955	0.033
C	-0.1011	-0.0358	A:	0.7135	1.2848	0.0343
			B:	0.7157	1.3199	0.0329

The correlation between charge and spin density of the main atoms of the ligand and metal center is shown in Fig. 7.

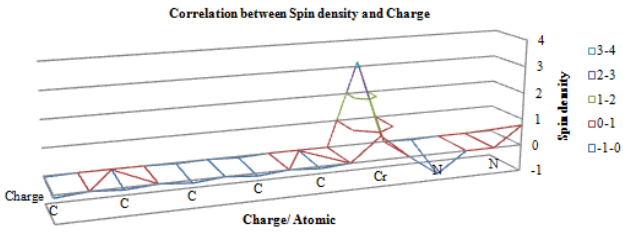

Fig. 7 The correlation between charge and spin density of **3**

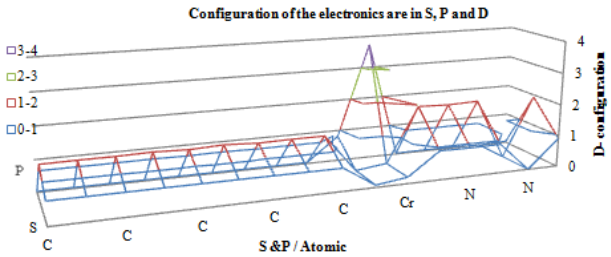

Fig. 8 The correlation of the electronics is in S& P and D of **3**

The most positive charge and spin density are in chromium (III) atom center as expected; this is as Lewis acid to electron pair acceptor the extra electron density. Again, α and β configuration of the electronics are in S, P and D orbitals of the complex **3** are presented in Fig. 8.

IV. CONCLUSION

The computational chemistry presented in this paper shows the possible to produce chromium (III) complexes incorporating the chelating diamido cyclopentadienyl $[Cr(ArN(CH_2)_3NAr)_2(\eta^5\text{-}Cp)]$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ and Cp= C_5H_5) from optimization information, via the Dewar-Chatt-

Duncanson model, as a basis of the molecular orbital (MO) analysis was showed the correlation between the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital LUMO has been showed, plus the energy diagram of the complex.

By using Mulliken population as indicate of Chromium(III) cyclopentadienyl the charges were found at 0.8928 for chromium and -0.7673 for each nitrogen atoms, from this point the overall more electron-rich nitrogen atoms can donated electrons density to from coordination bond to the less electron-rich chromium center atom leaving them with sigma and coordination bonds.

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