DFT Study of Half Sandwich of Vanadium (IV) Cyclopentadienyl Complexes

Salem El-tohami Ashoor

Abstract—A novel new vanadium (IV) complexes incorporating the chelating diamido cyclopentadienyl \([\text{ArN(CH}_3\text{)}_2\text{NAr}] Cl(\eta^5-\text{Cp})\) \((Ar = 2,6-\text{Pr}_2\text{C}_6\text{H}_3)\) \((Cp = \text{C}_2\text{H}_5\text{)}\text{n} = 1,2,3,4,\text{and} 5\) have been studied with calculation of the properties of species involved in various of cyclopentadienyl reaction. These were carried out under investigation of density functional theory (DFT) calculation, and comparing together. Other methods, explicitly including electron correlation, are necessary for more accurate calculations; MBSLYP (Becke) (Lee–Yang–Parr) level of theory often being used to obtain more exact results. These complexes were estimated of electronic energy for molecular system, because it accounts for all electron correlation interactions. The optimised of \([\text{V(=NAr)} Cl(\eta^5-\text{Cp})]\) \((Ar = 2,6-\text{Pr}_2\text{C}_6\text{H}_3)\) and \(Cp = \text{C}_2\text{H}_5\text{)}\text{n} = 1,2,3,4,\text{and} 5\) was found to be thermally more stable than others of vanadium cyclopentadienyl. In the meantime the complex \([\text{V(=NAr)} Cl(\eta^5-\text{Cp})]\) \((Ar = 2,6-\text{Pr}_2\text{C}_6\text{H}_3)\) and \(Cp = \text{C}_2\text{H}_5\text{)}\text{n} = 1,2,3,4,\text{and} 5\) which is showed a low thermal stability in case of the just one carbon of cyclopentadienyl can be incorporation with vanadium metal centre. 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—Vanadium(IV) cyclopentadienyl complexes, DFT, MO, HOMO, LUMO.

I. INTRODUCTION

During the past ten-years there is a dramatic development of the vanadium chemistry because of discoveries of many physiological [1], [2] and catalytic activities of its compounds [3]-[6]. To date, most of the Group 4 and Group 5 catalysts for polymerisation have been supported by one or more cyclopentadienyl rings, [7], [8] but there is a growing interest in the use of new ancillary, non cyclopentadienyl ligands, such as chelating diamides or diamido donor ligands, [9], [10] Vanadium(V) imido complex with cyclopentadienyl withes is the metal centre d0 can be obtained by reaction of vanadium (V) imido with trimethylseleylcyclopentadien to produce moderate air sensitive. Then this complex was reduced with magnesium in the presence of trimethylphosphine to yield \([\text{V(=NAr)Cp(PMe}_3\text{)}_2]\) and the phoshpine may be substituted by CO, ethylene or diphenylacetylene to give \([\text{V(=NAr)CpL}\] \((L = \text{CO, C}_2\text{H}_4, \text{PhC} (=\text{CPh})).[11]\)

II. METHOD

A complex of \([\text{V(=NAr)} Cl(\eta^5-\text{Cp})]\) \((Ar = 2,6-\text{Pr}_2\text{C}_6\text{H}_3)\) and \(Cp = \text{C}_2\text{H}_5\text{)}\text{n} = 1,2,3,4,\text{and} 5\) can be make via the reaction of \([\text{V(=NAr)} Cl(\eta^5-\text{Cp})]\) \((Ar = 2,6-\text{Pr}_2\text{C}_6\text{H}_3)\) and \(Cp = \text{C}_2\text{H}_5\text{)}\text{n} = 1,2,3,4,\text{and} 5\) in presence of NaCp at low temperature Fig. 1:

![Fig. 1 Preparation of \([\text{V(=NAr)} Cl(\eta^5-\text{Cp})]\) \((Ar = 2,6-\text{Pr}_2\text{C}_6\text{H}_3)\) and \(Cp = \text{C}_2\text{H}_5\text{)}\text{n} = 1,2,3,4,\text{and} 5\) via chemcraft from point group selection](image)

III. RESULT AND DISCUSSION

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

The DFT structure confirmed the constitution of 3, which shows CS symmetry. There is a mirror plane that divides the two chloride ligands through the vanadium centre (C(3)-V-C(5)Cp). The nitrogen donors chelate around the vanadium centre as expected, and the metal centre resides in a distorted tetrahedral environment defined by N, N’, Cl, and Cp (Fig. 2).

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From the point of comparable to the corresponding the optimizations for the spin density and bond energy under different points groups of the complexes [V(ArN(CH\textsubscript{2})\textsubscript{2}NAr\textsubscript{2}Cl(\eta\textsuperscript{-}C\textsubscript{p})], V(\textsubscript{1}ArN(CH\textsubscript{2})\textsubscript{2}NAr\textsubscript{2}Cl(\eta\textsuperscript{-}C\textsubscript{p})], [V(\textsubscript{1}ArN(CH\textsubscript{2})\textsubscript{2}NAr\textsubscript{2}Cl(\eta\textsuperscript{-}C\textsubscript{p})] and [V(\textsubscript{1}ArN(CH\textsubscript{2})\textsubscript{2}NAr\textsubscript{2}Cl(\eta\textsuperscript{-}C\textsubscript{p})] as showed in Table I. The lower energy was found to be as [V(\textsubscript{1}ArN(CH\textsubscript{2})\textsubscript{2}NAr\textsubscript{2}Cl(\eta\textsuperscript{-}C\textsubscript{p})] complex, which is sporting a final molecular structure of 3.

The chelate bite angle, defined by the N(1)-V-N(2) bond angle of 97.00\(^\circ\) derives from the short three-carbon bridge. The Cl-V-Cp bond angle is 104.282\(^\circ\) as shown in Fig. 3. As can be seen from the chemcraft publication 2 diagram, it displays similar features to that of Mono(cyclopentadienyl)vanadium alkynyl and aryne complexes of the previously work. [12]-[14]

Vanadium cyclopentadine bond lengths are showed in Table II in detail. 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 115.219\(^\circ\) around the metal centre < N(1)-V-N(2) as compared to the perversely work [15].

### Table I

**Selected Some Parameters of Spin Density and Bond Energy**

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<thead>
<tr>
<th>Complex</th>
<th>ADF</th>
<th>ADF</th>
<th>ADF</th>
<th>ADF</th>
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<tr>
<td>spin density</td>
<td>1.2988</td>
<td>1.2078</td>
<td>1.2067</td>
<td>1.0729</td>
<td>1.2883</td>
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<td>Bond Energy</td>
<td>-17.43281851 a.u.</td>
<td>-17.67244884 a.u.</td>
<td>-17.67244552 a.u.</td>
<td>-17.80954554 a.u.</td>
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<tr>
<td>Bond Energy</td>
<td>-474.37112790 eV</td>
<td>-480.89179322 eV</td>
<td>-484.62291978 eV</td>
<td>-476.65460147 eV</td>
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<tr>
<td>Bond Energy</td>
<td>-10939.26 kcal/mol</td>
<td>-11089.63 kcal/mol</td>
<td>-11089.6 kcal/mol</td>
<td>-11175.66 kcal/mol</td>
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</tr>
</tbody>
</table>

### Table II

**Selected Bond Lengths and Angles in 3**

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<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Fragment</th>
<th>Angle (°)</th>
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<tr>
<td>V-N(1)</td>
<td>1.91</td>
<td>N(2)-V-Cl</td>
<td>102.037</td>
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<td>V-N(2)</td>
<td>1.91</td>
<td>N(2)-V-N(1)</td>
<td>97.00</td>
</tr>
<tr>
<td>V-Cl</td>
<td>2.3</td>
<td>N(1)-V-Cl</td>
<td>102.037</td>
</tr>
<tr>
<td>V-Cp</td>
<td>2.0</td>
<td>N(2)-V-Cp</td>
<td>123.351</td>
</tr>
<tr>
<td>N(1)-C(4)</td>
<td>1.44</td>
<td>N(1)-V-Cp</td>
<td>124.488</td>
</tr>
<tr>
<td>N(2)-C(16)</td>
<td>1.44</td>
<td>Cp-V-Cl</td>
<td>104.282</td>
</tr>
<tr>
<td>N(1)-C(11)</td>
<td>1.47</td>
<td>C(4)-N(1)-V</td>
<td>127.497</td>
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</table>

Supporting Information of the frontier orbitals of HOMO and LUMO of the complex [V(\textsubscript{1}ArN(CH\textsubscript{2})\textsubscript{2}NAr\textsubscript{2}Cl(\eta\textsuperscript{-}C\textsubscript{p})] (\textsubscript{1}ArN(CH\textsubscript{2})\textsubscript{2}C\textsubscript{6}H\textsubscript{5} and Cp = C\textsubscript{5}H\textsubscript{5}) is shown in Fig. 5.
Fig. 5 Frontier orbitals of HOMO and LUMO of 3

IV. CONCLUSION

The computational chemistry presented in this paper shows that it is possible to produce vanadium (IV) complexes incorporating the chelating diamido cyclopentadienyl [V(AR(N(CH₂)₃)₂NAR)₂Cl(η⁵-C₅H₅)] (AR = 2,6-Pr₂C₆H₃ and Cp = C₅H₅) from optimization information. At meantime other possibilities were carry out, from the point to find the lowest energy. via the Dewar-Chatt-Duncanson model, as a basis of the molecular orbital (MO) analysis was showed the the correlation between the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital LUMO.

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REFERENCES


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