

# 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  $\{\text{ArN}(\text{CH}_2)_3\text{NAr}\}^{2-}(\eta^5\text{-Cp})$  (Ar = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$ ) ( $\text{Cp} = \text{C}_5\text{H}_5$  and  $n = 1, 2, 3, 4$  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; MB3LYP (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  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^5\text{-Cp})]$  (Ar = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$  and  $\text{Cp} = \text{C}_5\text{H}_5$ ) was found to be thermally more stable than others of vanadium cyclopentadienyl. In the meantime the complex  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^1\text{-Cp})]$  (Ar = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$  and  $\text{Cp} = \text{C}_5\text{H}_5$ ) which is showed a low thermal stability in case of the just one carbon of cyclopentadienyl can be insertion with vanadium metal centre. By using Dewar-Chart-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 ligands is the metal centre d0 can be obtained by reaction of vanadium (V) imido with trimethylsilylcyclopentadiene to produce moderately air sensitive. Then this complex was reduced with magnesium in the presence of trimethylphosphine to yield vanadium imido cyclopentadiene trimethylphosphine and the phosphine may be substituted by CO, ethylene or diphenylacetylene.[11].

The half-sandwich vanadium (V) imido complex  $[\text{V}(=\text{NAr})\text{CpCl}_2]$  can be obtained by reaction of  $[\text{V}(=\text{NAr})\text{Cl}_3]$  (Ar = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$ ) with  $\text{CpSiMe}_3$  to produce moderately air sensitive  $[\text{V}(=\text{NAr})\text{CpCl}_2]$  in good yield.  $[\text{V}(=\text{NAr})\text{CpCl}_2]$  can then be reduced with magnesium in the presence of

trimethylphosphine to yield  $[\text{V}(=\text{NAr})\text{Cp}(\text{PMe}_3)_2]$  and the phosphine may be substituted by CO, ethylene or diphenylacetylene to give  $[\text{V}(=\text{NAr})\text{CpL}]$  (L = CO,  $\text{C}_2\text{H}_4$ ,  $\text{PhC}\equiv\text{CPh}$ ).[11]

## II. METHOD

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

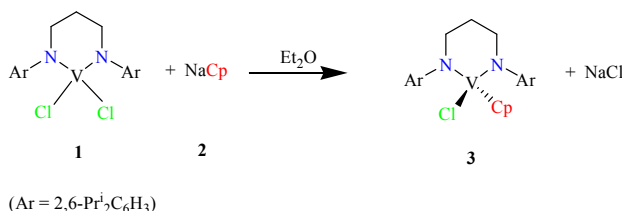


Fig. 1 Preparation of  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^5\text{-Cp})]$  (Ar = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$  and  $\text{Cp} = \text{C}_5\text{H}_5$ )

## III. RESULT AND DISCUSSION

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

The DFT structure confirmed the constitution of **3**, which shows  $\text{C}_s$  symmetry. There is a mirror plane that divides the two chloride ligands through the vanadium centre ( $\text{C}(3)\text{-V-C}(5)\text{Cp}$ ). 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).

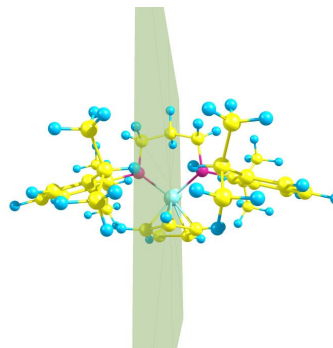


Fig. 2  $\text{C}_s$ -Symmetry of **3** via chemcraft from point group selection

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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  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^5\text{-Cp})]$ ,  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^4\text{-Cp})]$ ,  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^3\text{-Cp})]$ ,  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^1\text{-Cp})]$  and  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^1\text{-Cp})]$  as showed in Table I. The lower energy was found to be as  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^5\text{-Cp})]$  complex, which is sporting a final molecular structure of **3**.

( $\eta^2\text{-Cp}$ ) and  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^1\text{-Cp})]$  as showed in Table I. The lower energy was found to be as  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^5\text{-Cp})]$  complex, which is sporting a final molecular structure of **3**.

TABLE I  
SELECTED SOME PARAMETERS OF SPIN DENSITY AND BOND ENERGY

Complex	$[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^5\text{-Cp})]$ (Ar = 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$ and Cp = $\text{C}_5\text{H}_5$ )	$[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^4\text{-Cp})]$ (Ar = 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$ and Cp = $\text{C}_5\text{H}_5$ )	$[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^3\text{-Cp})]$ (Ar = 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$ and Cp = $\text{C}_5\text{H}_5$ )	$[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^2\text{-Cp})]$ (Ar = 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$ and Cp = $\text{C}_5\text{H}_5$ )	$[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^1\text{-Cp})]$ (Ar = 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$ and Cp = $\text{C}_5\text{H}_5$ )
spin density	1.2988	1.2078	1.2067	1.0729	1.2883
Bond Energy	-17.43281851 a.u.	-17.67244848 a.u.	-17.67244525 a.u.	-17.80954554 a.u.	-17.51673462 a.u.
Bond Energy	-474.37112790 eV	-480.89179120 eV	-480.89170322 eV	-484.62239197 eV	-476.65460147 eV
Bond Energy	-10939.26 kcal/mol	-11089.63 kcal/mol	-11089.6 kcal/mol	-11175.66 kcal/mol	-10991.92 kcal/mol
point group	Cs-Sym	NoSym	NoSym	NoSym	NoSym

The chelate bite angle, defined by the N(1)-V-N(2) bond angle of  $97.004^\circ$  derives from the short three-carbon bridge. The Cl-V-Cp bond angle is  $104.282^\circ$ , N(2)-V-Cl, N(1)-V-Cl, N(2)-V-Cp and N(1)-V-Cp bonds angles are  $102.037^\circ$ ,  $102.037^\circ$ ,  $123.351$  and  $124.488$  respectively.

The structure of **3** is 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]

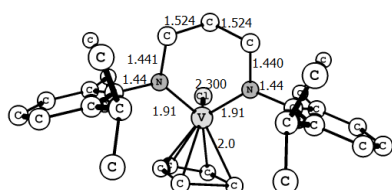


Fig. 3 Molecular structure of **3** via chemcraft publication 2

Vanadium cyclopentadiene 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 II  
SELECTED BOND LENGTHS AND ANGLES IN **3**

Bond	Length (Å)	Fragment	Angle (°)
V-N(1)	1.91	N(2)-V-Cl	102.037
V-N(2)	1.91	N(2)-V-N(1)	97.00
V-Cl	2.3	N(1)-V-Cl	102.037
V-Cp	2.0	N(2)-V-Cp	123.351
N(1)-C(4)	1.44	N(1)-V-Cp	124.488
N(2)-C(16)	1.44	Cp-V-Cl	104.282
N(1)-C(1)	1.47	C(4)-N(1)-V	127.497

The basis of the molecular orbital (MO) analysis is the Dewar-Chatt-Duncanson model, [16] which is can be used to the best describing the bonding of cyclopentadiene to the metal centre. Our spin-unrestricted BP86/TZVP calculations on the staggered and eclipsed model of  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^5\text{-Cp})]$  (Ar = 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$  and Cp =  $\text{C}_5\text{H}_5$ ) is in agreement with the previous DFT calculations, with the field spin-up of  $\alpha$  orbital at -4.6292eV and in field spin-down of  $\beta$  at -5.7351eV as shown in Fig. 4.

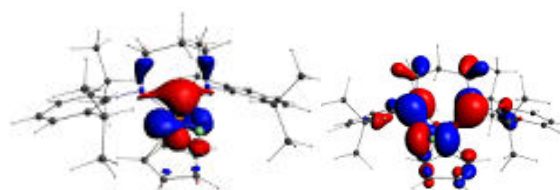


Fig. 4 HOMO of orbitals  $\alpha$  and  $\beta$

Supporting Information of the frontier orbitals of HOMO and LUMO of the complex  $[\text{V}(\text{ArN}(\text{CH}_2)_3\text{NAr})_2\text{Cl}(\eta^5\text{-Cp})]$  (Ar = 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$  and Cp =  $\text{C}_5\text{H}_5$ ) is shown in Fig. 5.

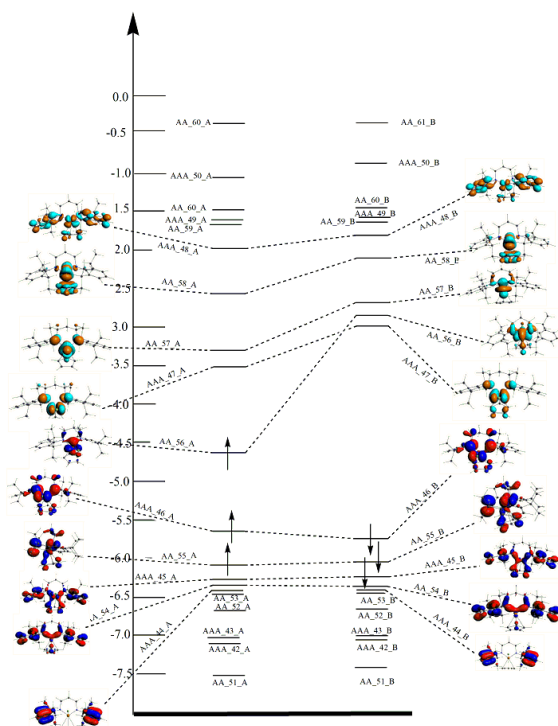


Fig. 5 Frontier orbitals of HOMO and LUMO of 3

#### IV. CONCLUSION

The computational chemistry presented in this paper shows that it is possible to produce vanadium (IV) complexes incorporating the chelating diamido cyclopentadienyl  $[V(ArN(CH_2)_3NAr)_2Cl(\eta^5-Cp)]$  ( $Ar = 2,6\text{-}Pr_2C_6H_3$  and  $Cp = C_5H_5$ ) 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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