# Imidazol-2-ylidene stabilized tetrahedral cobalt carbonyl complexes: A computational and structural database study

Samuel Tetteh [*]

*Department of Chemistry, School of Physical Sciences, College of Agriculture and Natural Sciences, University of Cape Coast, Cape Coast, Ghana*

## ARTICLE INFO

## ABSTRACT

A combined crystallographic database and computational chemistry analyses of tetrahedral cobalt (Co) carbonyl (CO) complexes bearing substituted imidazol-2-ylidene (Im) ligands were studied. These group of compounds are potential catalysts in the hydroformylation of alkenes as well as effective precursors for both chemical vapour deposition and atomic layer deposition in integrated circuit manufacture. A substructure search revealed seventeen (17) crystal structures in the Cambridge Structural Database (CSD). Generally, there was a positive correlation between the Im-Co bond length and the Co–CO bond length implying that a strong Im-CO bonding interaction could give rise to a more stable carbonyl complex. The gas phase structures of these complexes were further studied computationally at the BP86 level of the density functional theory. The def2-TZVPP basis set was used for cobalt with 6-31G (d,p) for all other atoms. It was observed that the Co–CO bond length increased with increase in bulkiness of alkyl substituents at the *ortho* positions of the Im ligands. Subsequent natural bond orbital (NBO) and chemical reactivity parameter analyses revealed that the chemical softness, electronic chemical potential and the ease of ionization also increased with increase in bulkiness of the alkyl substituents. This property has useful applications in catalytic systems and for the design of precursors in integrated circuit manufacture.

## 1. Introduction

Cobalt complexes are among the most important compounds used in homogeneous processes catalyzed by transition metals. Since the discovery of cobalt catalyzed hydroformylation by Otto Roelen [1] in 1938, millions of tons of carbonyls and alcohols are produced from alkenes, hydrogen gas (H₂) and carbon monoxide (CO) each year [2]. According to Heck and Breslow [3], the active catalytic species HCo(CO)₃, a 16-electron species in which the central Co is tetracoordinated with see-saw shape and Cs symmetry has the hydrido and one carbonyl ligand in axial positions with the remaining two CO ligands in equatorial positions. This coordinatively unsaturated geometry makes it easier for the attachment of the alkene to begin the hydroformylation reaction [4]. Despite the success of the HCo(CO)₃ catalyzed hydroformylation reaction, few problems still arise; these include (a) the low linear/branched aldehyde ratios, instability and difficulty in recovery of the active catalyst and (b) the high partial pressure (200–300 atm) of CO and its associated cost required to build and operate these catalytic units [2].

These challenges were however improved with the addition of tertiary phosphine ligands such as tributyphosphine (PBu₃). The introduction of this bulky and electron rich ligand improved the linear/branched

aldehyde ratio [5] as well as stabilized the Co–CO bond by significantly reducing the operating CO partial pressures needed for the catalytic process. The observed stability of the Co–CO bond is as a result of the greater electron donating ability of the PBu₃ ligand. This increases the π-back-bonding ability of Co into empty CO π* orbitals which strengthens the Co–CO bond [6]. Steric factors have also been invoked to account for the higher proportion of the anti-Markovnikov products as a result of the larger cone angle of PBu₃ [7].

N-Heterocyclic carbenes (NHCs) have gained prominence as ubiquitous ligands in organometallic and coordination chemistry because of their diverse electronic and steric properties [8, 9]. Notable among these carbenes are the five-membered imidazol-2-ylidene (Im) rings [9]. These heterocycles have an sp² hybridized divalent carbon atom in-between two sp² hybridized nitrogen atoms. The bonding mode of NHCs towards transition metals have been the subject of current research, both theoretically and experimentally [10, 11]. Spectroscopic studies have shown the ligating modes of NHCs to be similar to those of alkylphosphines and alkylphosphites, both ligands being σ-donors with low π-back-bonding character [9, 12]. The frontier orbitals of NHCs are made up of doubly occupied sp² hybridized orbitals and an empty orthogonal pπ orbital with interactions similar to Fischer type carbene complexes in
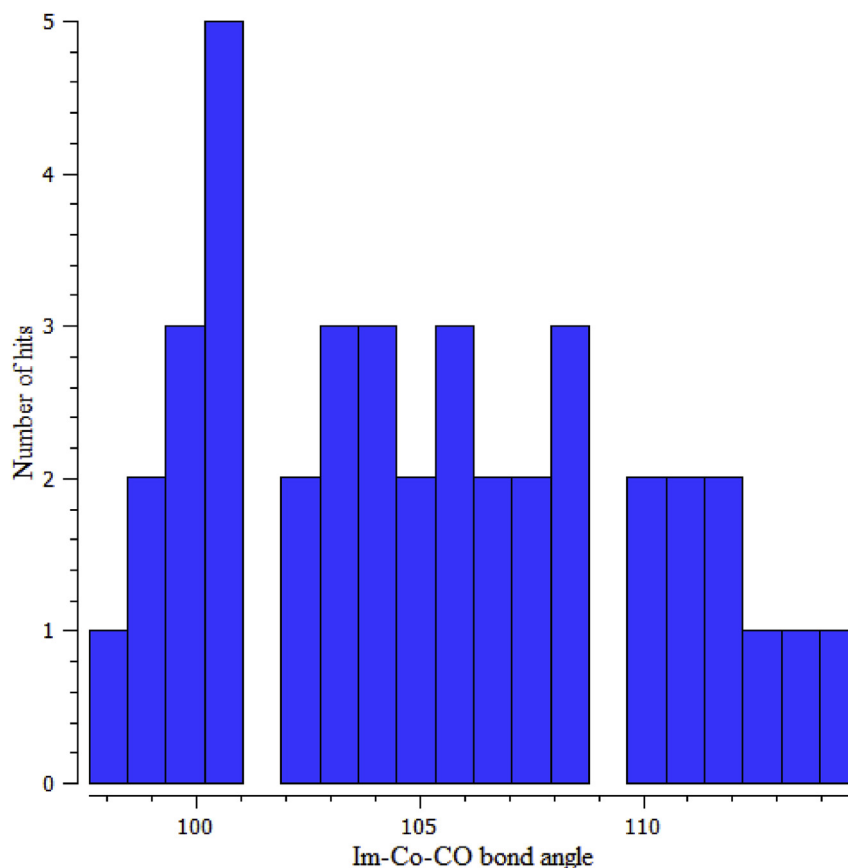
---

**Fig. 1.** Distribution of the imidazole cobalt carbonyl bond angles in the cobalt complexes retrieved from the database.

which the lone pair of electrons in the $sp^2$ orbital is donated to the d-orbital of the metal [13]. However, because of the weak π-acceptor ability of the empty pπ orbital, the transition metal (TM)-NHC bond is largely represented as a single bond, a phenomenon which has been confirmed experimentally [14]. The empty pπ orbital however contributes to the aromaticity of the imidazole ring by accepting electrons from adjacent nitrogen atoms in respective canonical structures. Studies by Lin *et al* have reported that π-electron delocalization in the NHC ring does not affect its donor ability and that for NHC complexes, σ-donation is predominant over π-back-bonding [8]. However, Khramov *et al*, have also shown that the π-back-bonding ability of imidazol-2-ylidenes can be tuned by changing the π-acidity of substituents on the imidazole ring [15].

The introduction of substituents on the N atoms of imidazol-2-ylidene has been found to greatly increase its stability. The first stable NHC isolated by Arduengo *et al* had adamantyl groups as substituents on the N atoms. The stability of this compound was attributed to the steric hindrance of these substituents which protected the free ligand from dimerization [9]. Other analogues with mesityl and isopropyl substituted benzenes have shown remarkable stabilities and have been isolated as free NHCs. The imidazole ring can also be stabilized by using substituents such as Cl which can donate π-electrons to increase the electron density on the NHC ring. This variation of substituents on the N atoms can be used to fine tune the electronic and steric properties of specific imidazol-2-ylidene [15].

This work looks at the effect of alkyl substituents on the N atoms of imidazole-2-ylidene cobalt (II) carbonyl nitrosyl complexes considering the fact that NHC ligands are good σ-donors and sterically bulky to enhance the stabilization of the Co–CO bond in the presence of electron withdrawing NO ligands. Recent reports have also shown NHC stabilized cobalt complexes to be effective precursors for both chemical vapour deposition (CVD) and atomic layer deposition (ALD) in integrated circuit

manufacture [16]. Based on the importance and growing interest in the use of NHC stabilized cobalt complexes, this study surveys the number and properties of tetrahedral cobalt carbonyl complexes in the Cambridge structural Database (CSD) with particular emphasis on the Co–CO and Co-Im bond lengths. Global chemical reactivity descriptors such as chemical hardness (η), electronic chemical potential (μ), electrophilicity (ω), ionization energy (I) and the significance of the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Imidazol-2-ylidene stabilized cobalt carbonyl complexes are also studied computationally using the density functional theory (DFT).

## 2. Methodology

### 2.1. Computational methods

All calculations were performed with the Gaussian09 software [17]. The input files were also prepared using the GaussView 5.0.8 molecular structure viewer [18]. The gas phase structures were fully optimized without symmetry constraints at the density functional theory (DFT) using Becke 1988 exchange functional [19] and Perdew 86 correlation functional (BP86) [19, 20]. This functional has been found to be a robust choice for the study of cobalt complexes [21]. Effective core potentials (ECPs) were used to represent the valence electrons of cobalt and a triple-ζ basis set associated with pseudopotentials known as def2-TZVPP [22]. The 6-31G (d,p) basis set was used for all other atoms. Vibrational frequency analysis of the structures was used to confirm the stationary points on the potential energy surface and there were no imaginary frequencies [23]. The computational methods were validated by comparing the bond parameters with those of respective crystal structures in the Cambridge Structural Database (CSD) [24]. Natural bond orbital (NBO) analysis was used to estimate the net atomic charges of selected atoms
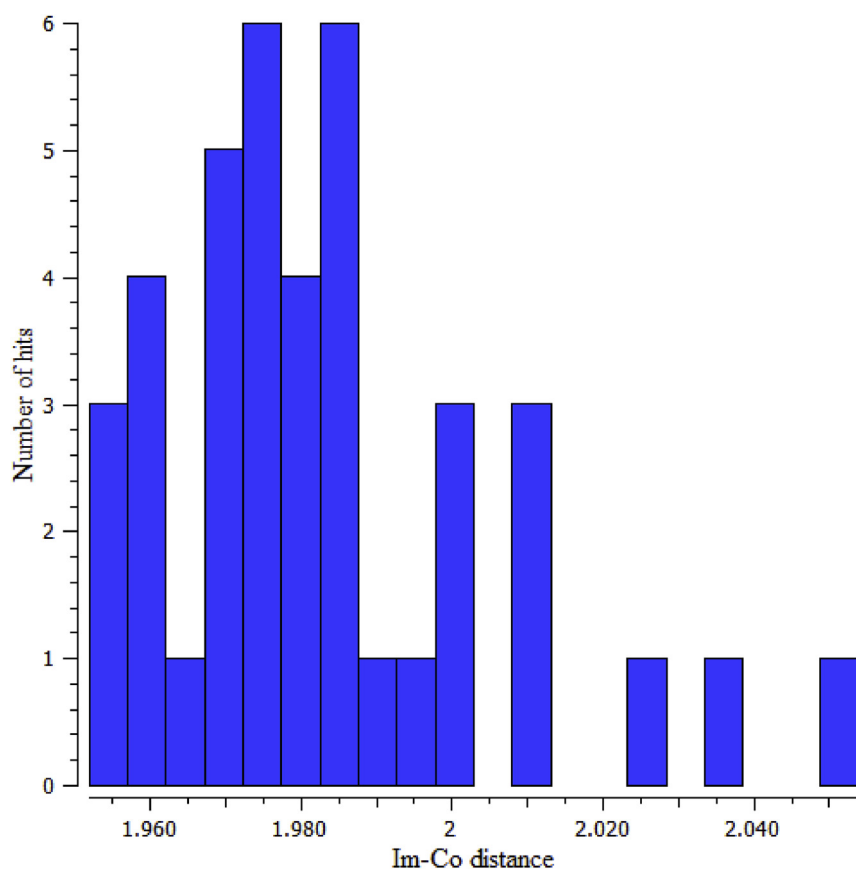
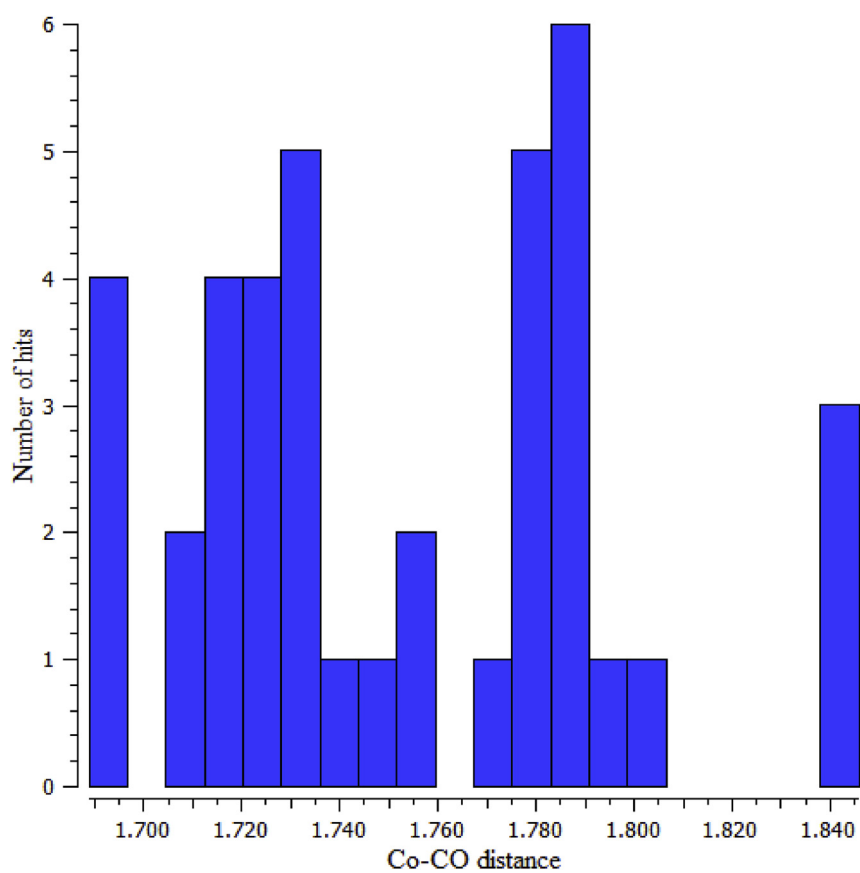**Fig. 2.** Distribution of imidazol-2-ylidene-cobalt bond distances in the complexes retrieved from the CSD.



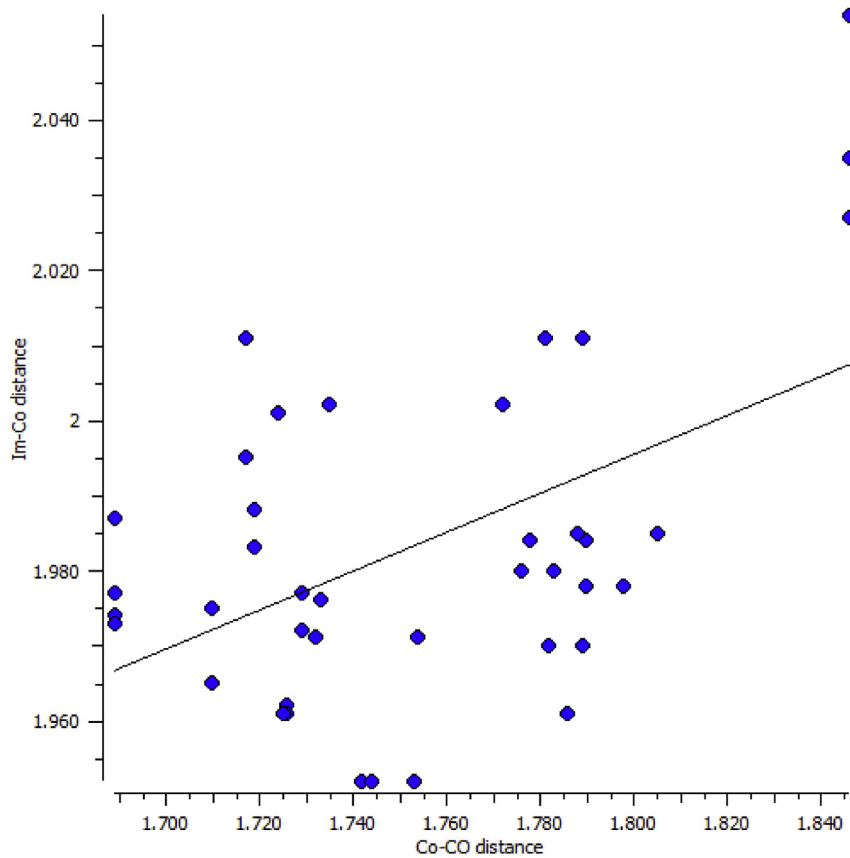**Fig. 3.** Distribution of Co–CO bond lengths in the complexes retrieved from the database.

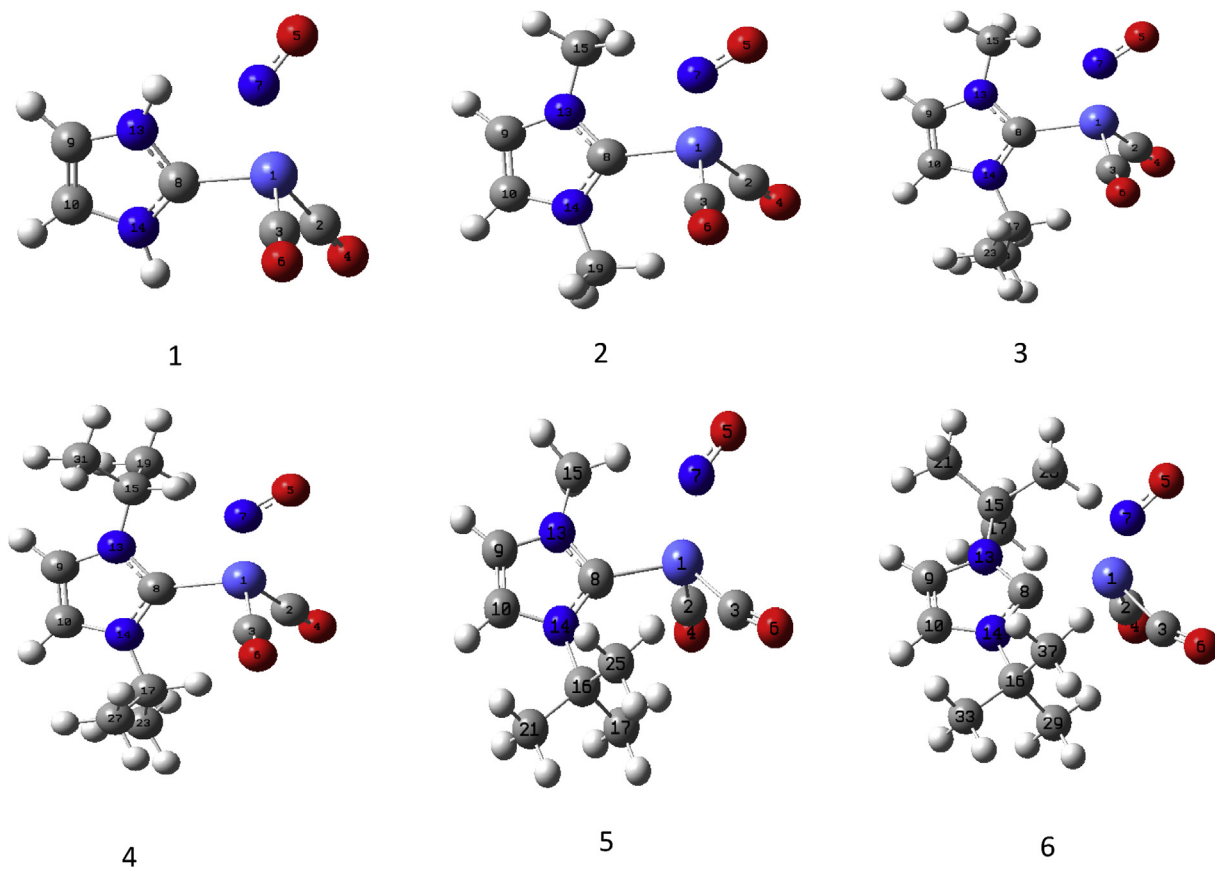**Fig. 4.** A scatter plot of the correlation between the Im-Co bond lengths and Co–CO bond lengths.



**Fig. 5.** Gas phase optimized structures of complexes 1 to 6.

**Table 1**
Selected bond lengths (Å) and angles (°) of the optimized structures.

| Parameter | 1 | 2(OVUZOW) | 3 | 4(OVUQIZ) | 5(OWABEV) | 6 |
|---|---|---|---|---|---|---|
| Co (1)-C (2) | 1.834 | 1.836 (1.754) | 1.835 | 1.835 (1.778) | 1.832 (1.781) | 1.830 |
| Co (1)-C (3) | 1.857 | 1.870 (1.732) | 1.870 | 1.871 (1.790) | 1.874 (1.789) | 1.907 |
| Co (1)-N (7) | 2.007 | 2.002 (1.733) | 2.005 | 2.007 (1.665) | 2.002 (1.654) | 2.004 |
| Co (1)-C (8) | 1.972 | 2.007 (1.971) | 2.009 | 2.011 (1.984) | 2.042 (2.011) | 2.059 |
| N (7)-O (5) | 1.242 | 1.242 (1.150) | 1.242 | 1.242 (1.173) | 1.244 (1.171) | 1.240 |
| C (2)-O (4) | 1.162 | 1.162 (1.144) | 1.162 | 1.162 (1.137) | 1.161 (1.140) | 1.163 |
| C (3)-O (6) | 1.157 | 1.158 (1.149) | 1.159 | 1.159 (1.142) | 1.159 (1.139) | 1.160 |
| C (8)-Co (1)-N (7) | 92.74 | 106.69 (104.71) | 106.83 | 107.07 (117.37) | 102.66 (123.13) | 102.98 |
| C (8)-Co (1)-C (2) | 104.01 | 100.95 (110.01) | 100.68 | 100.62 (99.96) | 99.19 (100.30) | 100.21 |
| C (8)-Co (1)-C (3) | 103.98 | 105.37 (106.80) | 106.45 | 106.29 (100.73) | 116.53 (100.60) | 119.14 |
| C (2)-Co (1)-C (3) | 101.03 | 103.37 (108.6) | 103.24 | 103.51 (108.41) | 100.98 (107.26) | 97.75 |
| C (2)-Co (1)-N (7) | 147.71 | 140.87 (110.7) | 141.12 | 141.22 (111.74) | 143.04 (112.24) | 150.16 |
| C (3)-Co (1)-N (7) | 101.41 | 95.47 (115.6) | 94.81 | 94.29 (116.82) | 95.45 (111.24) | 87.14 |
| Co (1)-N (7)-O (5) | 127.72 | 123.73 (177.03) | 123.52 | 123.80 (174.61) | 123.99 (171.09) | 127.37 |
| Co (1)-C (3)-O (6) | 174.14 | 168.45 (175.1) | 168.58 | 168.24 (177.60) | 166.27 (175.40) | 161.59 |

[25]. Frontier molecular orbitals (FMOs) were also investigated at the same level of theory. All atomic coordinates of the optimized structures have been added as Supplementary information (S1 to S6).

### 2.2. CSD analysis

Version 5.39 (November 2017) plus one update of the CSD was assessed for this study. This version contains over 900 000 structural entries. Substructure searches of tetra-coordinated imidazol-2-ylidene cobalt carbonyl complexes were performed with the CSD System program *ConQuest* version 1.20 employing the following search filters: atomic coordinates determined; no disordered and error files; no polymeric nor ionic fractions; only organometallic (according to standard CSD definitions). The CSD program *Mercury* (version 3.10) was used for the structural visualization while the statistical analysis of the retrieved data was performed using the Data Analysis Module implemented within the *Mercury* package.

### 3. Results and discussion

A CSD substructure search using *ConQuest* version 1.20 revealed seventeen (17) tetra-coordinated crystal structures of imidazole-2-ylidene stabilized cobalt carbonyl complexes. As shown in Fig. 1, the geometry of the coordinated ligands (Im-Co-CO bond angle) around the central cobalt is generally tetrahedral [26] with bond angles ranging from 97.62° to a maximum of 114.83° with an average of 105.3°. The slight differences can be attributed to steric interactions as well as intermolecular interactions within the crystal lattice.

Fig. 2 shows the distribution of Im-Co bond distances in the studied complexes. The bond lengths range from 1.952 Å in the crystal structure with refcode HIDYUQ [27] to 2.054 Å in RAJFOY [28]. The mean and standard deviations were found to be 1.983 Å and 0.022 respectively. HIDYUQ is a dimesiytl substituted imidazole-2-ylidene stabilized cobalt dicarbonyl complex. The introduction of 1,3,5-trimethylbenzene substituents on the N-atoms of Im does not only increase the steric bulkiness around the ligand but also increases the electron density on the imidazole ring and contributes to its π-electron donor ability thereby decreasing the Im-Co bond length. Similar observations have been reported by Arduengo [29] who worked on a series of (1,3-dimesitylimidazol-2-ylidene)$_2$M (M = Ni, Pt) complexes. Subsequently, the longest bond length in RAJFOY is as a result of fewer electron donating groups on the imidazole ring such that the bonding mode of the imidazole ring to the central cobalt atom is purely by σ-donation with reduced π-interaction [15].

Generally, a high electron density on a metal ion increases its back-bonding ability [30]. For a metal-carbonyl bond, this property strengthens the bond and leads to a more stable complex [31]. As shown in Fig. 3, the Co–CO bond distances range from 1.689 Å in OWAMOQ [16], to a maximum of 1.846 Å in RAJFOY [28] with mean and standard

deviation of 1.757 Å and 0.037 respectively.

As shown in Fig. 4, a positive correlation is observed between the imidazole-cobalt bond distances and the cobalt-carbonyl bond distances. This means that generally, the longer the Im-Co distance, the weaker the Co–CO bond. A shorter Im-Co bond formed as a result of substantial imidazole-to-carbonyl π-bonding leads to an increase in electron density on the cobalt ion. The cobalt ion then donates these extra electrons into antibonding orbitals of the carbonyl ligand.

This metal-to-ligand back-bonding decreases the Co–CO bond distance and stabilizes the CO ligand. A phenomenon which has been attributed largely to the Dewar-Chatt-Duncanson model of synergic bonding in which a drift of electron density from the metal d-orbitals into π* CO antibonding orbitals decreases the metal-carbonyl bond and weakens the C–O bond [32]. Therefore processes that would have occurred at high CO partial pressures can now occur at reduced pressures which is more economical for industries.

According to Khramov et al [15], the ability of the central metal to donate dπ-electrons into empty CO-pπ* orbitals depends strongly on the type of ancillary ligands present. π-acidic or π-basic ligands compete with the CO ligand for metal dπ electrons or augment the π-interaction between the metal and the CO as a result of increased electron density on the metal. These interactions have been studied spectroscopically and in all cases, the M-C bond length either increases or decreases based on the type of ancillary ligand and the type of substituent it contain [33, 34]. To better understand the effect of ancillary ligands on the observed bond parameters in the CSD, six cobalt complexes containing alkyl substituted imidazol-2-ylidene, carbonyl and nitrosyl ligands were fully optimized as shown in Fig. 5.

Three of these optimized structures were compared to complexes with refcodes OVUZIQ, OWABEV and OVUZOW [16] in the CSD shown in Table 1. The slight differences could be attributed to the fact that intermolecular and lattice interactions are stronger in the crystal than in the gas phase optimized structures. From the results, the Im-Co bond is seen

**Table 2**
Natural Charge (e) distribution in the gas phase optimized complexes.

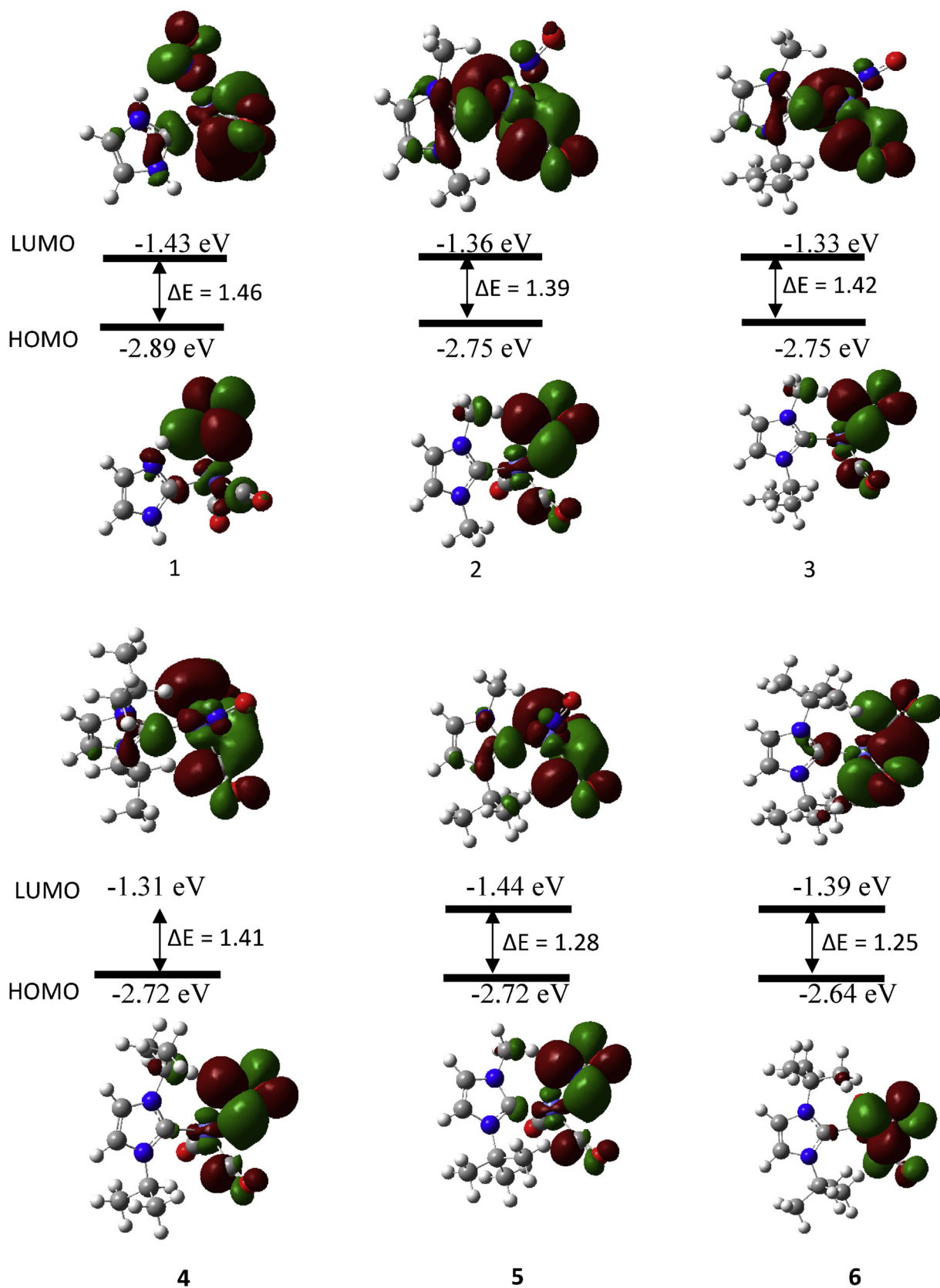| Natural charge (e) | | | | | | |
|---|---|---|---|---|---|---|
| Atom | 1 | 2 | 3 | 4 | 5 | 6 |
| Co (1) | −0.144 | −0.151 | −0.150 | −0.157 | −0.156 | −0.177 |
| C (2) | +0.501 | +0.501 | +0.504 | +0.504 | +0.511 | +0.508 |
| C (3) | +0.547 | +0.524 | +0.520 | +0.520 | +0.509 | +0.490 |
| O (4) | −0.412 | −0.412 | −0.414 | −0.414 | −0.412 | −0.418 |
| O (5) | −0.248 | −0.254 | −0.255 | −0.256 | −0.266 | −0.262 |
| O (6) | −0.405 | −0.407 | −0.408 | −0.409 | −0.403 | −0.404 |
| N (7) | −0.197 | −0.164 | −0.163 | −0.158 | −0.146 | −0.126 |
| C (8) | +0.209 | +0.228 | +0.227 | +0.229 | +0.220 | +0.224 |
| N (13) | −0.548 | −0.375 | −0.383 | −0.378 | −0.375 | −0.383 |
| N (14) | −0.561 | −0.380 | −0.374 | −0.384 | −0.387 | −0.383 |

Fig. 6. Frontier orbitals of complexes 1 to 6.

**Table 3**
Global chemical reactivity indices for the optimized structures.

|  | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Energy (hartree) | −728.16 | −809.79 | −855.44 | −964.09 | −924.75 | −1042.71 |
| E (LUMO) (eV) | −1.43 | −1.36 | −1.33 | −1.31 | −1.44 | −1.39 |
| E (HOMO) (eV) | −2.89 | −2.75 | −2.75 | −2.72 | −2.72 | −2.64 |
| ΔE (Gap) | 1.46 | 1.39 | 1.41 | 1.41 | 1.28 | 1.25 |
| Chemical hardness (η) | 0.73 | 0.69 | 0.71 | 0.71 | 0.64 | 0.63 |
| Chemical softness | 1.37 | 1.44 | 1.41 | 1.42 | 1.56 | 1.60 |
| Electron. Chem potential (μ) | −2.16 | −2.05 | −2.04 | −2.01 | −2.08 | −2.01 |
| Electrophilicity (ω) | 3.20 | 3.04 | 2.94 | 2.87 | 3.39 | 3.24 |
| Ionization energy (I) | 2.89 | 2.75 | 2.75 | 2.72 | 2.72 | 2.64 |
| Eelectron affinity (A) | 1.43 | 1.36 | 1.33 | 1.31 | 1.44 | 1.39 |
| Total dipole moment (μD) | 7.53 | 8.35 | 8.38 | 8.14 | 8.12 | 8.12 |

to increase with increase in the size of the substituents on the imidazole ligand. It increased from 1.972 Å in **1** to 2.059 Å in **6**.

Generally, NHCs are considered two electron σ-donor ligands with an empty p-orbital on the atom available for π-back-bonding. The donation of dπ-electrons from the Co atom into this empty orbital is expected to decrease the Co–NHC bond length if the ancillary ligands were electron donating [15]. Unfortunately all the ligands are π-acid ligands and compete strongly for the Co-dπ electrons. The observed increase in bond length has been attributed to the increase in steric bulkiness at the *ortho*-positions of the NHC which enforces minor elongation of the Co–C (8) bond [16]. Consequently, the C (8)-Co (1)-N (7) and C (8)-Co (1)-C (3) bond angles increase with corresponding decrease in the Co(2)-Co (1)-C (3) angle. The Co (1)–C (2), Co (1)–C (3) and Co (1)–N (7) bond lengths did not show any appreciable changes. The Natural bond orbital (NBO) charge distribution on representative atoms is shown in Table 2. It can be seen that the charge density on Co (1) increased from -0.144 to -0.177 e across the series. In a similar order, the electronic charge on the carbene carbon decreased from +0.209 to +0.228. This shows that the σ-donor ability of the carbene carbon is partly responsible for the increase in electron density on cobalt [35]. The hyperconjugative effect of the alkyl groups on N (13) and N (14) could also be responsible for the increase in electron density on Co (1) across the series [36]. The carbonyl carbons, C (2) and C (3) did not show any significant changes in charge density but there were slight decreases in the case of N (7) from **1** to **6**.

The frontier orbitals are important indicators in the electronic structure of a molecule [37]. The energy of the highest occupied molecular orbitals (HOMO) is usually associated with the ionization energy of a molecule. Molecules with higher HOMO energies easily donate electrons in bonding interactions.

On the other hand, the energy of the lowest unoccupied molecular orbital shows the ability of a molecule to accept electrons [38]. The smaller the HOMO-LUMO gap, the easier it is to promote electrons from a donor molecular orbital to an acceptor orbital. In the case of these Co(II) complexes, the HOMO is a singly occupied molecular orbital (SOMO). From Fig. 6, the HOMO is largely centered on the central Co whereas the LUMO is ligand based. Also, the energy of the HOMO steadily increased from -2.89 to -2.64 eV across the series with a corresponding increase in the energy of the LUMO from -1.43 to -1.39 eV. However, the energy of the HOMO-LUMO gap decreased from 1.46 to 1.25 across the same series. According to the Koopman's theorem, the energy of the frontier orbitals can be used to estimate chemical reactivity parameters such as chemical hardness (η), chemical softness (s), electronic chemical potential (μ), electrophilicity (ω), ionization energy (I) as well as electron affinity (A) [39, 40].

As shown in Table 3, the chemical softness increased from 1.37 for **1** to 1.60 for **6** which corresponds to the increments observed in the energy of the HOMO. This order shows that the introduction of bulky substituents at the N (13) and N (14) positions of the imidazole ligand increases the donor ability of the complex with corresponding decrease in η. Similar trends were also observed in the ionization energies and electron affinities of the complex.

The electronic chemical potential describes the ability of electrons to escape from an equilibrium system [41]. The smaller the value of μ, the more stable the complex. From Table 3, μ increases from −2.16 to −2.01 across the same series, confirming the ease of ionization and chemical softness of the complexes.

## 4. Conclusion

Imidazole-2-ylidene stabilized tetrahedral cobalt carbonyl complexes are a group of promising transition metal complexes with varied applications. The σ-donor and π-donor properties of the imidazole ring enhances the stability of the cobalt-carbonyl bond and decreases the high partial pressures of carbon monoxide required for cobalt carbonyl catalyzed processes such as hydroformylation. This paper assessed the stability of tetrahedral imidazole-2-ylidene stabilized cobalt carbonyl complexes. A substructure search of the Cambridge Structural Database (CSD) version 5.39 (November 2017) plus one update revealed seven (17) crystal structures of cobalt carbonyl complexes with substituted imidazol-2-ylidenes. Generally, there was a positive correlation between the imidazole-2-ylidene-cobalt bond distance and the cobalt-carbonyl bond distance. Implying that a shorter Im-Co bond distance results in a more stable Co–CO bond thereby stabilizing the CO ligand. Studies of the electronic structure of the complexes at the density functional level of theory also revealed that the chemical softness, electronic chemical potential and the ease of ionization increased with increase in bulkiness of the substituents on the imidazol-2-ylidene ligand.

Crystallographic Data Center (CCDC) for assess to the Cambridge Structural Database (CSD) for substructure searches and Statistical Analysis.

# References

[1] J. Falbe, Carbon Monoxide in Organic Synthesis, vol 10, Springer Science & Business Media, 2013.

[2] F. Hebrard, P. Kalck, Cobalt-catalyzed hydroformylation of alkenes: generation and recycling of the carbonyl species, and catalytic cycle, Chem. Rev. 109 (9) (2009) 4272–4282.

[3] R.F. Heck, D.S. Breslow, The reaction of cobalt hydrotetracarbonyl with olefins, J. Am. Chem. Soc. 83 (19) (1961) 4023–4027.

[4] G.O. Spessard, G.L. Miessler, Organometallic Chemistry, 2009.

[5] C. Brown, G. Wilkinson, Homogeneous hydroformylation of alkenes with hydridocarbonyltris-(triphenylphosphine) rhodium (I) as catalyst, J. Chem. Soc. A Inorg. Phys. Theor. (1970) 2753–2764.

[6] R.K. Hocking, T.W. Hambley, Database analysis of transition metal carbonyl bond lengths: insight into the periodicity of π back-bonding, σ donation, and the factors affecting the electronic structure of the TM− C⋮O moiety, Organometallics 26 (11) (2007) 2815–2823.

[7] N. Mathew, B.R. Jagirdar, R.S. Gopalan, G. Kulkarni, Influence of the cone angles and the π-acceptor properties of phosphorus-containing ligands in the chemistry of dihydrogen complexes of ruthenium, Organometallics 19 (22) (2000) 4506–4517.

[8] J.C. Lin, R.T. Huang, C.S. Lee, A. Bhattacharyya, W.S. Hwang, I.J. Lin, Coinage metal− N-heterocyclic carbene complexes, Chem. Rev. 109 (8) (2009) 3561–3598.

[9] H. Jacobsen, A. Correa, A. Poater, C. Costabile, L. Cavallo, Understanding the M (NHC)(NHC= N-heterocyclic carbene) bond, Coord. Chem. Rev. 253 (5-6) (2009) 687–703.

[10] L. Cavallo, A. Correa, C. Costabile, H. Jacobsen, Steric and electronic effects in the bonding of N-heterocyclic ligands to transition metals, J. Organomet. Chem. 690 (24-25) (2005) 5407–5413.

[11] X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, Group 11 metal complexes of N-heterocyclic carbene ligands: nature of the metal carbene bond, Organometallics 23 (4) (2004) 755–764.

[12] K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, Mehrfachbindungen zwischen hauptgruppenelementen und übergangsmetallen: CXXVI. Heterocyclen-carbene als phosphananaloge liganden in metallkomplexen, J. Organomet. Chem. 459 (1-2) (1993) 177–184.

[13] C.D. Abernethy, G.M. Codd, M.D. Spicer, M.K. Taylor, A highly stable N-heterocyclic carbene complex of trichloro-oxo-vanadium (V) displaying novel Cl− Ccarbene bonding interactions, J. Am. Chem. Soc. 125 (5) (2003) 1128–1129.

[14] K.F. Donnelly, A. Petronilho, M. Albrecht, Application of 1, 2, 3-triazolylidenes as versatile NHC-type ligands: synthesis, properties, and application in catalysis and beyond, Chem. Commun. 49 (12) (2013) 1145–1159.

[15] D.M. Khramov, V.M. Lynch, C.W. Bielawski, N-heterocyclic carbene− transition metal complexes: spectroscopic and crystallographic analyses of π-back-bonding interactions, Organometallics 26 (24) (2007) 6042–6049.

[16] F. Hering, J.H. Berthel, K. Lubitz, U.S. Paul, H. Schneider, M. Hrterich, U. Radius, Synthesis and thermal properties of novel NHC-stabilized cobalt carbonyl nitrosyl complexes, Organometallics 35 (17) (2016) 2806–2821.

[17] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, Gaussian 09, Revision A. 1 [computer Software], Gaussian, Wallingford, CT, USA, 2009.

[18] R.D. Dennington, T.A. Keith, J.M. Millam, GaussView 5.0. 8, Gaussian Inc, 2008.

[19] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Phys. Rev. A 38 (6) (1988) 3098.

[20] J.P. Perdew, Erratum: density-functional approximation for the correlation energy of the inhomogeneous electron gas, Phys. Rev. B 34 (10) (1986) 7406.

[21] K.P. Jensen, J. Cirera, Accurate computed enthalpies of spin crossover in iron and cobalt complexes, J. Phys. Chem. A 113 (37) (2009) 10033–10039.

[22] F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy, Phys. Chem. Chem. Phys. 7 (18) (2005) 3297–3305.

[23] S. Tetteh, R. Zugle, Theoretical study of terminal vanadium (V) chalcogenido complexes bearing chlorido and methoxido ligands, J. Chem. 2017 (2017) 8.

[24] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, The Cambridge structural database, Acta Crystallogr. B: Struct. Sci., Cryst. Eng. Mater. 72 (2) (2016) 171–179.

[25] E. Glendening, A. Reed, J. Carpenter, F. Weinhold, Nbo Version 3.1, Tci, University of Wisconsin, Madison 65, 1998.

[26] G.M. Battle, G.M. Ferrence, F.H. Allen, Applications of the Cambridge structural database in chemical education, J. Appl. Crystallogr. 43 (5) (2010) 1208–1223.

[27] J.A. Przyojski, H.D. Arman, Z.J. Tonzetich, NHC complexes of cobalt (II) relevant to catalytic C–C coupling reactions, Organometallics 32 (3) (2012) 723–732.

[28] X. Hu, I. Castro-Rodriguez, K. Meyer, Dioxygen activation by a low-valent cobalt complex employing a flexible tripodal N-heterocyclic carbene ligand, J. Am. Chem. Soc. 126 (41) (2004) 13464–13473.

[29] A.J. Arduengo III, S.F. Gamper, J.C. Calabrese, F. Davidson, Low-coordinate carbene complexes of nickel (0) and platinum (0), J. Am. Chem. Soc. 116 (10) (1994) 4391–4394.

[30] G. Kuppuraj, M. Dudev, C. Lim, Factors governing metal− ligand distances and coordination geometries of metal complexes, J. Phys. Chem. B 113 (9) (2009) 2952–2960.

[31] C.K. Kim, K.A. Lee, C.K. Kim, B.-S. Lee, H.W. Lee, NBO analyses of the back-bonding in metal–olefin complexes, Chem. Phys. Lett. 391 (4-6) (2004) 321–324.

[32] D.M.P. Mingos, A historical perspective on Dewar's landmark contribution to organometallic chemistry, J. Organomet. Chem. 635 (1-2) (2001) 1–8.

[33] X. Hu, I. Castro-Rodriguez, K. Meyer, Synthesis and characterization of electron-rich nickel tris-carbene complexes, Chem. Commun. (19) (2004) 2164–2165.

[34] M.D. Sanderson, J.W. Kamplain, C.W. Bielawski, Quinone-annulated N-heterocyclic carbene− transition-metal complexes: observation of π-backbonding using FT-IR spectroscopy and cyclic voltammetry, J. Am. Chem. Soc. 128 (51) (2006) 16514–16515.

[35] C. Lee, C.S. Vasam, T. Huang, H. Wang, R. Yang, C. Lee, I.J. Lin, Silver (I) N-heterocyclic carbenes with long N-alkyl chains, Organometallics 25 (15) (2006) 3768–3775.

[36] V. Pophristic, L. Goodman, Hyperconjugation not steric repulsion leads to the staggered structure of ethane, Nature 411 (6837) (2001) 565.

[37] G. Frenking, Understanding the nature of the bonding in transition metal complexes: from Dewar's molecular orbital model to an energy partitioning analysis of the metal–ligand bond, J. Organomet. Chem. 635 (1-2) (2001) 9–23.

[38] C. Boehme, J. Uddin, G. Frenking, Chemical bonding in mononuclear transition metal complexes with Group 13 diyl ligands ER (E= B- Tl): Part X: theoretical studies of inorganic compounds, Coord. Chem. Rev. 197 (1) (2000) 249–276.

[39] C.A. Mebi, DFT study on structure, electronic properties, and reactivity of cis-isomers of [(NC 5 H 4-S) 2 Fe (CO) 2], J. Chem. Sci. 123 (5) (2011) 727–731.

[40] R. Vargas, J. Garza, A. Cedillo, Koopmans-like approximation in the Kohn− Sham method and the impact of the frozen core approximation on the computation of the reactivity parameters of the density functional theory, J. Phys. Chem. A 109 (39) (2005) 8880–8892.

[41] C. Morell, A. Grand, A. Toro-Labbe, New dual descriptor for chemical reactivity, J. Phys. Chem. A 109 (1) (2005) 205–212.