

Quantum chemical investigation for structures and bonding analysis of molybdenum tetracarbonyl complexes with N-heterocyclic carbene and analogues: helpful information for plant biology research

Khảo sát cấu trúc và phân tích bản chất liên kết của phức $Mo(CO)_4$ chứa phối tử N-heterocyclic carbene và các phức tương tự bằng tính toán hóa lượng tử: Thông tin hữu ích cho các nghiên cứu về sinh học thực vật

Research article

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Quantum chemical calculations at the gradient-corrected (BP86) density-functional calculations with various basis sets (SVP, TZVPP) have been carried out for $Mo(CO)_4$ complexes of N-heterocyclic carbene and analogues-NHE_{Me} (called tetrylenes) with E = C, Si, Ge, Sn, Pb. The equilibrium structures of complexes $[Mo(CO)_4-NHE_{Me}]$ ($Mo4-NHE_{Me}$) exhibit an interesting trend which the lightest adduct $Mo4-NHC_{Me}$ has a trigonal bipyramidal coordination mode where the ligand NHC_{Me} occupies an equatorial position. In contrast, the heavier species from $Mo4-NHSi_{Me}$ to $Mo4-NHPb_{Me}$ possess a square pyramidal structure where the ligands from NHSi_{Me} to NHPb_{Me} occupy a basal position. The slighter complexes $Mo4-NHE_{Me}$ possess end-on-bonded NHE_{Me} ligands when E = C, Si, Ge with the bending angles, α , are 180° whereas the heavier adducts $Mo4-NHSn_{Me}$ and $Mo4-NHPb_{Me}$ exhibit strongly side-on-bonded ligands which the bending angle, α become more acute. The trend of the bond dissociations energies- D_e [kcal/mol] (BDEs) for the Mo-E bonds is $Mo4-NHC_{Me} > Mo4-NHSi_{Me} > Mo4-NHGe_{Me} > Mo4-NHSn_{Me} > Mo4-NHPb_{Me}$. Bonding analysis shows that the Mo-E bonds have a significant contribution from $(CO)_4Mo \leftarrow NHE_{Me} \pi$ -donation. This is because the energy levels of the π -type donor orbitals of $Mo4-NHC_{Me} - Mo4-NHPb_{Me}$ are higher lying than the σ -type donor orbitals. The NHE_{Me} ligands in $Mo4-NHE_{Me}$ are strong electron donors. This review intends to provide a comprehensive data for plant biology research in the future.

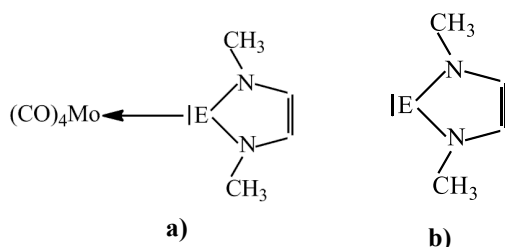
Tính toán hóa lượng tử sử dụng lý thuyết phiếm hàm mật độ kết hợp điều chỉnh gradient (BP86) từ các bộ hàm cơ sở khác nhau (SVP, TZVPP) được thực hiện cho việc tính toán lý thuyết của phức giữa $Mo(CO)_4$ và phối tử N-heterocyclic carbene và các phức tương tự NHE_{Me} (gọi là tetrylenes) với E = C, Si, Ge, Sn, Pb. Cấu trúc của phức $[Mo(CO)_4-NHE_{Me}]$ ($Mo4-NHE_{Me}$) thể hiện sự khác biệt khá thú vị từ $Mo4-NHC_{Me}$ đến $Mo4-NHPb_{Me}$, phức $Mo4-NHC_{Me}$ có cấu trúc phối trí lưỡng tháp tam giác trong đó phối tử NHC_{Me} chiếm ở vị trí xích đạo. Ngược lại, những phức có phân tử khối lớn hơn từ $Mo4-NHSi_{Me}$ đến $Mo4-NHPb_{Me}$ lại có cấu trúc tháp vuông và các phối tử từ NHSi_{Me} đến NHPb_{Me} chiếm vị trí cạnh (basal – cạnh hướng về bốn đỉnh của đáy vuông). Các cấu trúc của phức $Mo4-NHE_{Me}$ cho thấy các phối tử NHE_{Me} với E = C-Ge tạo với phân tử $Mo(CO)_4$ một góc thẳng $\alpha = 180.0^\circ$, ngược lại, các phức nặng hơn $Mo4-NHE_{Me}$

thì phối tử NHE_{Me} với $E = Sn, Pb$ liên kết với phân tử $Mo(CO)_4$ tạo góc cong và góc cong, α , càng trở nên nhọn hơn khi nguyên tử khối của E càng lớn. Năng lượng phân ly liên kết của liên kết $Mo-E$ giảm dần: $Mo4-NHC_{Me} > Mo4-NHSi_{Me} > Mo4-NHGe_{Me} > Mo4-NHSn_{Me} > Mo4-NHPb_{Me}$. Phân tích liên kết $Mo-E$ cho thấy có sự đóng góp đáng kể của sự cho liên kết π $(CO)_4Mo \leftarrow NHE_{Me}$. Điều này có thể do mức năng lượng của orbital π -cho của $Mo4-NHC_{Me} - Mo4-NHPb_{Me}$ nằm cao hơn orbital σ -cho. Từ kết quả tính toán có thể kết luận rằng phối tử NHE_{Me} trong phức $Mo4-NHE_{Me}$ là chất cho điện tử mạnh. Kết quả nghiên cứu lý thuyết về hệ phức $Mo4-NHE_{Me}$ lần đầu tiên cung cấp một cơ sở dữ liệu hoàn chỉnh cho các nghiên cứu về sinh học thực vật trong tương lai.

Keywords: tetrylenes, bond dissociation energy (BDE), density functional calculations, bonding analysis, end-on-bonded ligands, side-on-bonded ligands

1. Introduction

Quantum chemical calculations of the unknown carbodienes $C(NHC)_2$ with NHC is N-heterocyclic carbene which possess an unusual $C \leftarrow C$ donor-acceptor bond of a divalent carbon(II) atom can acts as σ donor were performed in the recent past [15]. Transition metal complexes with NHC ligands [4] and related systems [10], as well as those with the heavier homologues NHE where $E = Si, Ge, Sn, Pb$ have been extensively studied [18]. This is because NHCs ligands are excellent catalysts in various chemical reactions [16]. Recently, Bertrand and co-workers [2] attached successfully carbenes to metals to form metal-carbene complexes that serve as efficient catalysts used widely in the environmental researches by using green methods. Besides, it has been found that the importance of molybdenum for plant growth is disproportionate with respect to the absolute amount required by most plants [8]. Molybdenum is a transition element, which can exist in several oxidation states ranging from zero to VI, where VI is the most common form found in most agricultural soils with the most stable being Mo^{+4} ($Mo(IV)$) and Mo^{+6} ($Mo(VI)$). It has been mentioned that similar to most metals required for plant growth such as iron, copper, zinc, manganese, and boron, molybdenum has been utilized by specific plant enzymes to participate in reduction and oxidative reactions [17]. The new findings suggest that it would be worth investigating the $Mo(CO)_4$ complexes that carries NHE_{Me} ligands where $E = C - Pb$, which may exist, but have not yet been synthesized.



Scheme 1. Schematic representation of: a) complexes $Mo4-NHE_{Me}$ and b) ligands NHE_{Me} with $E = C - Pb$

Those motivate us to choose $[(CO)_4Mo-\{NHE_{Me}\}]$ ($Mo4-NHE_{Me}$) complexes to study in order to see whether the interesting bonding situation between $Mo(CO)_4$ and N-heterocyclic carbene-analogues, which is revealed by the bonding analysis has any unusual bonding mode to their

chemical behavior. Herein, we report on quantum chemical calculations using density functional theory (DFT-BP86) to investigate $Mo4-NHE_{Me}$ complexes and fragments which are shown in Scheme 1. The electronic structure of the molecules was analyzed with charge method. The first detailed preparation of $[(CO)_4Mo-\{NHE_{Me}\}]$ complexes may provide helpful information for plant biology research.

2. Computational details

Geometry optimizations of the molecules in this paper were carried out without symmetry constraints using the Gaussian 03 [9] optimizer together with Turbomole 6.0.1 [14] energies and gradients at the BP86 [3] /def2-SVP [6] level of theory. For the heavier group-14 atoms Sn and Pb, and the Mo element of $Mo(CO)_4$, a small-core quasi-relativistic effective core potentials (ECPs) were used [1]. The RI approximation will be used for all structure optimizations by using the appropriate auxiliary basis sets. The convergence criterion for the SCF energy is set to 10^{-8} a.u and the modified integration grid "m4" was used. All structures presented in this study were turned out to the minima on the potential energy surface (PES). The nature of the stationary points on the PES was also confirmed as energy minima by frequency calculations. Bond-dissociation energy (BDE) or D_e is one measure of the strength in a chemical bond. For instance, the bond dissociation energy, D_e [kcal/mol], for a bond $(CO)_4Mo-NHE_{Me}$ which is broken through the reaction: $[Mo(CO)_4-\{NHE_{Me}\}] \rightarrow (CO)_4Mo + NHE_{Me}$ of a molecule $[Mo(CO)_4-NHE_{Me}]$ and formed from the two fragments $E^0[(CO)_4Mo]$ and $E^0[NHE_{Me}]$, is given by: $\Delta E = E[Mo(CO)_4-\{NHE_{Me}\}] - E^0[(CO)_4Mo] - E^0[NHE_{Me}] = -D_e$. For BDEs calculations, the parent compounds and free ligands were firstly optimized then the level of theory is denoted as BP86/def2-TZVPP[6]//BP86/def2-SVP for the calculation of the bond dissociation energies using the NBO 3.1 program [11].

The development of approximate density functional theory (DFT) approaches that accurately model the chemically very important dispersion interactions is a very active field of research as called DFT-D3. Dispersion interactions can be empirically defined as the attractive part of the van der Waals (vdW)-type interaction potential between atoms and molecules that are not directly bonded to each other. The complexes investigated in this study have

to be considered for dispersion interaction to affirm that these interactions might have an influence on the calculated results, especially on the theoretically predicted BDEs. The effect of dispersion interaction on the calculated bond dissociation energies was checked which is estimated with the DFT-D3 dispersion correction suggested by Grimme [5]. In order to get important conclusions about the effect interactions between ligands and substituted complexes, the calculated BDEs, D_e [kcal/mol], with and without corrections for dispersion interactions for the complexes were calculated at the BP86/def2-TZVPP and BP86/def2-TZVPP-D3 levels using BP86/def2-SVP-optimized geometries.

Single point calculations with the same functional with geometry optimizations (BP86) but the larger def2-TZVPP [7] basis set and small-core quasi-relativistic effective core potentials (ECPs) for the heavier atoms Sn and Pb were carried out with Gaussian 03 [9] on the structures derived on BP86/def2-SVP level of theory. In these calculations, the RI approximation was not used. The level of theory is denoted as BP86/def2-TZVPP // BP86/def2-SVP and used for the calculation of the Wiberg bond orders, natural partial charges, and for plotting molecular orbitals and orbital energies which was analyzed using the natural bond orbital (NBO 3.1 program) method available in Gaussian 03.

3. Results

3.1. Geometries, energies, and dispersion corrections

The optimized geometries of compounds $[\text{Mo}(\text{CO})_4\text{-NHE}_{\text{Me}}]$ (**Mo4-NHE_{Me}**) and free ligands NHE_{Me} together with calculated values for the most important bond lengths and angles at the BP86/def2-SVP level are shown in Figure 1 and Figure 2. There are no experimental values available for the complexes **Mo4-NHC_{Me}** to **Mo4-NHPb_{Me}**. The calculated Mo-NHC_{Me} bond length of **Mo4-NHC_{Me}** gives the shortest value (2.244 Å) and increases from **Mo4-NHC_{Me}** to **Mo4-NHPb_{Me}** (2.974 Å). This can be easily explained by the increasing radii of the group-14 atoms and the $\text{Mo}(\text{CO})_4$ molecule is a 14-electron specie which could act a 4-electron acceptor, resulting in an 18-electron complex. The equilibrium structures of **Mo4-NHC_{Me}**, **Mo4-NHSi_{Me}**, and **Mo4-NHGe_{Me}** have the NHE_{Me} ligands bonded in a head-on way to the tungsten atom which bending angles, α , is 180.0°. In the structures of **Mo4-NHSn_{Me}**, the NHSn_{Me} ligands are bonded in a side-on manner with the bending angles is 145.2°. The strongest side-on-bonded ligand when E = Pb has a bending angle, α , of 99.5°. The lightest adduct **Mo4-NHC_{Me}** has a

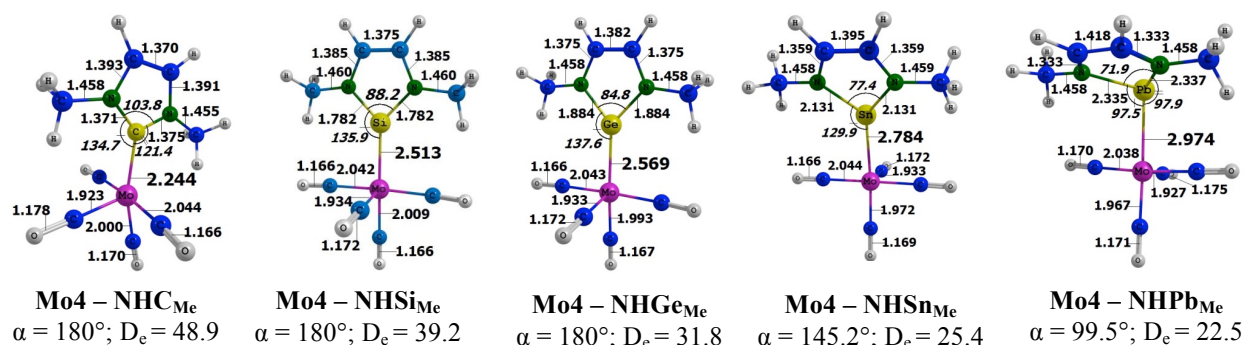


Figure 1. Optimized geometries of the complexes **Mo4-NHE_{Me}** at the BP86/def2-SVP level. Bond lengths are given in Å; angles in degrees. Calculated metal-ligand bond dissociation energies, D_e , at the BP86/def2-TZVPP//BP86/def2-SVP level for the $(\text{CO})_4\text{Mo-NHE}_{\text{Me}}$ bonds in kcal/mol. The bending angle, α , is the angle Mo-E-X where X is the midpoint between the N-N distance:

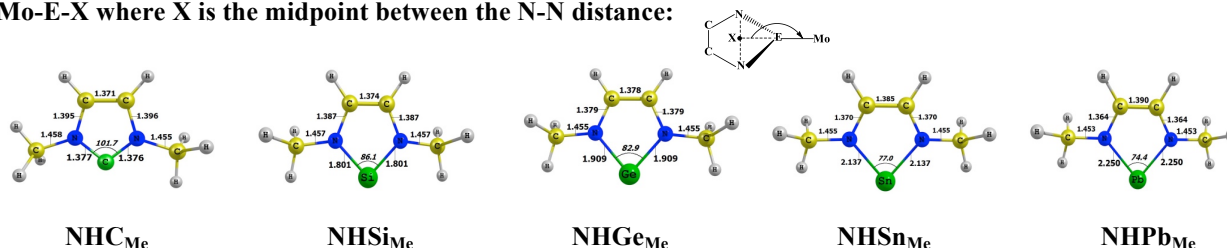


Figure 2. Optimized geometries of the fragment NHE_{Me} at the BP86/def2-SVP level. Bond lengths are given in Å; angles in degrees

trigonal bipyramidal coordination mode where the ligand NHC_{Me} occupies an equatorial position. In contrast, the heavier species from **Mo4-NHSi_{Me}** to **Mo4-NHPb_{Me}** possess a square pyramidal structure where the ligands from NHSi_{Me} to NHPb_{Me} occupy a basal position. Figure 1 and Figure 2 also show that the E-N bonds of the free NHE_{Me} ligands becomes slightly longer in the complexes **Mo4-NHE_{Me}** where E = C, Si, Ge, and Sn while they

become longer in the strongest side-on-bonded complex **Mo4-NHPb_{Me}**. Figure 1 gives the theoretical predicted BDEs for the Mo-E bonds of **Mo4-NHC_{Me}** to **Mo4-NHPb_{Me}**. There is a significantly decrease from the carbene complex **Mo4-NHC_{Me}** ($D_e = 48.9$ kcal/mol) to the silylene **Mo4-NHSi_{Me}** complex ($D_e = 39.2$ kcal/mol) and continuous decrease for the BDEs of the heavier homologues (48.9 – 22.5 kcal/mol). The BDEs results suggest

that the NHC_{Me} ligand in $\text{Mo4-NHC}_{\text{Me}}$ is the strongest bonded while the heavier complexes $\text{Mo4-NHSi}_{\text{Me}}$ to $\text{Mo4-NHPb}_{\text{Me}}$ have weaker bonds [12, 13].

Table 1. Calculated bond dissociation energies D_e [kcal/mol] with and without corrections for dispersion interactions for the complexes $\text{Mo4-NHE}_{\text{Me}}$

Compound	BP86/TZVPP	BP86/TZVPP	ΔE
	$-D_e$	$-D_3$	
$\text{Mo4-NHC}_{\text{Me}}$	48.9	60.2	11.3
$\text{Mo4-NHSi}_{\text{Me}}$	39.2	49.1	9.9
$\text{Mo4-NHGe}_{\text{Me}}$	31.8	40.7	8.9
$\text{Mo4-NHsn}_{\text{Me}}$	25.4	33.7	8.3
$\text{Mo4-NHPb}_{\text{Me}}$	22.5	34.0	11.4

Table 1 shows the theoretical BDEs with and without dispersion interactions for the complexes to $\text{Mo4-NHE}_{\text{Me}}$ which were calculated at the BP86/def2-TZVPP and BP86/def2-TZVPP-D3 levels using BP86/def2-SVP optimized geometries. The calculated BDE for the complex $\text{Mo4-NHPb}_{\text{Me}}$ becomes uniformly larger by 11.4 kcal/mol when dispersion interaction is considered; this is because of the strongest side-on bonded ligand NHPb_{Me} . A significantly larger value is calculated for carbene complex $\text{Mo4-NHC}_{\text{Me}}$ ($\Delta E = 11.3$ kcal/mol) which may due to the shortest Mo-C bond that makes the more bulky ligand which comes from the attractive forces between the CH_3 groups of free ligands and $\text{Mo}(\text{CO})_4$ fragment. In contract to this, the calculated BDEs for the complexes $\text{Mo4-NHE}_{\text{Me}}$ becomes uniformly smaller when E become heavier: *i*) The rather constant values for $\text{Mo4-NHGe}_{\text{Me}}$ and $\text{Mo4-NHsn}_{\text{Me}}$ ($\Delta E = 8.9$ and 8.3 kcal/mol) except for the slightly larger BDE value ($\Delta E = 9.9$ kcal/mol) in $\text{Mo4-NHSi}_{\text{Me}}$ which are shown by the longer bonds Mo-E compared with Mo-C bond in for $\text{Mo4-NHC}_{\text{Me}}$ adduct; *ii*) The complex $\text{Mo4-NHsn}_{\text{Me}}$ does not bring the large BDE value when dispersion correction is considered due to the slightly side-on-bonded ligand NHSn_{Me} . From this, it can be followed that the Mo-E bonds become longer for the heavier systems but the pair coefficients that are employed to calculate the strength of the dispersion interactions increase as: *iii*) The slighter atom with the Mo-C shortest bond in the head-on-bonded ligand of $\text{Mo4-NHC}_{\text{Me}}$; and *iv*) The heavier atom with the Mo-Pb longest bond in the strongest side-on-bonded ligand of $\text{Mo4-NHPb}_{\text{Me}}$. Thus, although the calculated BDEs of $\text{Mo4-NHE}_{\text{Me}}$ with the inclusion of dispersion interaction do not agree with the conclusion that the Mo-E bonds of the ligands NHE_{Me} becomes stronger for the heavier atoms but the calculated results affirmed that dispersion corrections have an influence on the theoretically predicted bond dissociation energies.

3.2. Bonding analysis

Table 2. NBO results with Wiberg bond indices (WBI) and natural population analysis (NPA) at the BP86/def2 – TZVPP//BP86/def2-SVP level for complexes $\text{Mo4-NHC}_{\text{Me}}$ – $\text{Mo4-NHPb}_{\text{Me}}$ and fragments. The partial charges, q , are given in electrons [e]

Molecule	Bond	WBI	$q[\text{Mo}(\text{CO})_4]$	Atom	q (NPA)
$\text{Mo4-NHC}_{\text{Me}}$	Mo – C	0.72	-0.47	Mo	-1.40

The bonding situation in compounds $\text{Mo4-NHE}_{\text{Me}}$ was analyzed using natural bond orbital (NBO) analysis. Table 2 gives results of the NBO calculations for parent compounds $\text{Mo4-NHC}_{\text{Me}}$ – $\text{Mo4-NHPb}_{\text{Me}}$ and for free ligands NHC_{Me} – NHPb_{Me} . The calculated partial charges show that the $\text{Mo}(\text{CO})_4$ fragment in the complexes always carries a negative charge, which slightly increases from $\text{Mo4-NHC}_{\text{Me}}$ (-0.47 e) to $\text{Mo4-NHPb}_{\text{Me}}$ (-0.64 e). It becomes obvious that charge donation is not directly related to bond strength of the donor-acceptor bond. The Wiberg bond order for the Mo-C bond in $\text{Mo4-NHC}_{\text{Me}}$ is much smaller (0.72) than that in heavier homologues where the values are almost constant between 0.90 for $\text{Mo4-NHSi}_{\text{Me}}$ and 0.84 for $\text{Mo4-NHGe}_{\text{Me}}$. The smallest value is given for the $\text{Mo4-NHPb}_{\text{Me}}$ (0.50) and stays nearly the same in $\text{Mo4-NHsn}_{\text{Me}}$ (0.73) compared with the Mo-C bond in complex $\text{Mo4-NHC}_{\text{Me}}$. Note that the bond order for the E-N bond becomes significantly smaller in the complexes $\text{Mo4-NHC}_{\text{Me}}$ – $\text{Mo4-NHPb}_{\text{Me}}$ than in the free ligands NHC_{Me} – NHPb_{Me} . Table 2 also gives the atomic partial charges of the donor atoms E and the acceptor atom Mo in the complexes $\text{Mo4-NHE}_{\text{Me}}$. The molybdenum atom always carries a large negative charge between -1.40 e (E = C) and -1.68 e (E = Si). The E donor atom has a positive charge of 0.30 e in $\text{Mo4-NHC}_{\text{Me}}$, and becomes more positively charged in the heavier atoms between 0.98 e (E = Pb) and 1.42 e (E = Si). Although the partial charges do not consider much the topography of the charge distribution but at least would suggest that the electrostatic interactions of the Mo-E bonds in $\text{Mo4-NHE}_{\text{Me}}$ have attractive electrostatic Mo-E interactions. The results of NBO analysis, it can be followed that neither charge distributions nor the bond orders correlates with the bond dissociation energies. However, the trend of the partial charges may support the suggestion that there is a change from ligand donation $[\text{Mo}] \leftarrow \text{E}$ for the head-on-bonded lighter homologues to metal donation $[\text{Mo}] \rightarrow \text{E}$ for the side-on-bonded species in complexes. The NBO analysis at least suggests that the the NHE_{Me} ligands are strong σ -donors and weak π -acceptors. This is possible for the ligands NHE_{Me} have only one lone-pair orbital available for donation [12]. From this, it can be realized that there is an important question of the bonding analysis of the compounds $\text{Mo4-NHE}_{\text{Me}}$ concerns the strength of the π donation $(\text{CO})_4\text{Mo} \leftarrow \text{NHE}_{\text{Me}}$ which may be expected from the π lone-pair orbital of the ligands NHE_{Me} into the second vacant coordination side of $\text{Mo}(\text{CO})_4$. Since the molecules have C_1 symmetry with no genuine σ and π orbitals since there is no mirror plane in the molecular structure. Therefore, the structures were optimized again with bending angles for all system are 180.0° (in one plane of molecules) and then visual inspection of the shape of the orbitals can easily identify σ -type and π -type molecular orbitals in complexes.

	C – N ₁	1.27		C	0.30
	C – N ₂	1.25		N	-0.30
NHC_{Me}	C – N ₁	1.27		C	0.04
	C – N ₂	1.26		N	-0.35
Mo4–NHSi_{Me}	Mo – Si	0.90	-0.71	Mo	-1.68
	Si – N ₁	0.78		Si	1.42
	Si – N ₂	0.78		N	-0.70
NHSi_{Me}	Si – N ₁	0.80		Si	0.84
	Si – N ₂	0.80		N	-0.71
Mo4–NHGe_{Me}	Mo – Ge	0.84	-0.66	Mo	-1.63
	Ge – N ₁	0.74		Ge	1.31
	Ge – N ₂	0.74		N	-0.67
NHGe_{Me}	Ge – N ₁	0.76		Ge	0.84
	Ge – N ₂	0.76		N	-0.70
Mo4–NHSn_{Me}	Mo – Sn	0.73	-0.63	Mo	-1.56
	Sn – N ₁	0.65		Sn	1.23
	Sn – N ₂	0.65		N	-0.63
NHSn_{Me}	Sn – N ₁	0.71		Sn	0.83
	Sn – N ₂	0.71		N	-0.67
Mo4–NHPb_{Me}	Mo – Pb	0.50	-0.64	Mo	-1.41
	Pb – N ₁	0.52		Pb	0.98
	Pb – N ₂	0.52		N	-0.52
NHPb_{Me}	Pb – N ₁	0.70		Pb	0.79
	Pb – N ₂	0.70		N	0.64

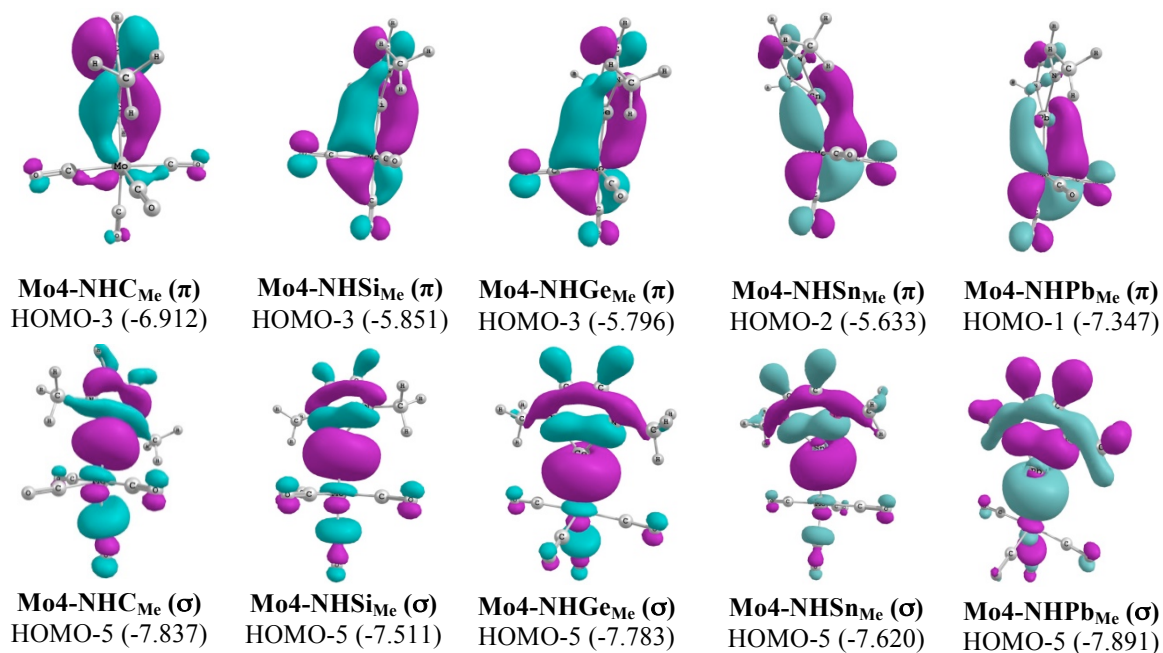


Figure 3. Molecular orbitals and orbital energies of σ -type and π -type MOs from **Mo4-NHC_{Me}** to **Mo4-NHPb_{Me}** at the BP86/TZVPP level. Orbital energies are given in eV

Figure 3 shows two occupied orbitals of the complexes which can be associated with $(\text{CO})_4\text{Mo} \leftarrow \text{NHE}_{\text{Me}}$ σ donation and π donation. This should be checked whether or not the π donation might be important in the complexes. The energy levels of the π -type donor orbitals of **Mo4-NHC_{Me}** – **Mo4-NHPb_{Me}** are higher lying than the σ -type donor orbitals. From this, it follows that the shape of the MOs indicate that $(\text{CO})_4\text{Mo} \leftarrow \text{NHE}_{\text{Me}}$ π donation is important in the complexes **Mo4-NHE_{Me}**. The analysis of the bonding situation gives the W-E bonds have a significant contribution from $(\text{CO})_4\text{Mo} \leftarrow \text{NHE}_{\text{Me}}$ strong σ -donation and strong π -donation. This can be explained

that the $\text{Mo}(\text{CO})_4$ molecule is a 14-electron specie and lacks a 4-electron acceptor. Although the ligands NHE_{Me} only retain one lone pair at E atom but the nitrogen in the NHE_{Me} ring can acts as ligands which indicate $\text{N} \rightarrow \text{E}$ donation and the NHE_{Me} ligands have the resonance form for molecules that can be realized because of the orbital overlap between the π -type lone pair and the $\text{N-E } \pi^*$ -orbitals which exhibits in more electron density at E atom. This makes the donor ligands NHE_{Me} can transfer more than one lone pair of electrons to the acceptor fragment $\text{Mo}(\text{CO})_4$.

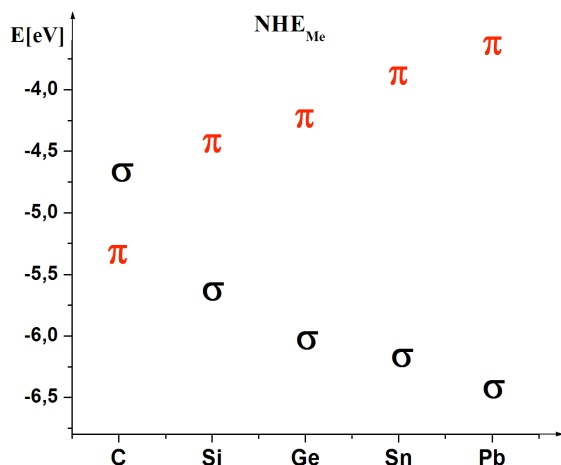


Figure 4. Plot of the energy levels of the highest-lying σ and π orbitals of NHE_{Me} ligands

The above results gives an insight into the nature of the bonding but they do not yet answer questions about the reason for the trend of the bond strength and the preference of heavier ligands for side-on bonding. Therefore, the calculated data was further analyzed to rationalize the theoretically predicted trends of the theory BP86/def2-TZVPP//BP86/def2-SVP level used for plotting the highest lying occupied orbital energies of free ligands NHE_{Me} . Figure 4 graphically shows the energy levels of the two highest lying occupied MOs which have σ or π symmetry of the ligands NHE_{Me} . It is clear to show that, in NHE_{Me} , the energy level of the π orbital rises, whereas the σ orbital becomes lower in energy when atom E becomes heavier. The trend of the energy levels of the energetically highest lying σ and π orbitals of NHE_{Me} rationalize the preference of the heavier ligands for a side-on coordination to the Mo atom, where $(CO)_4Mo \leftarrow E$ σ -donation takes places through the π orbital of the ligand [12]. The end-on and side-on coordination of the lighter and heavier homologues NHE_{Me} can be explained by various factors that also influence the bending angle, α , of the ligands. The binding over the π orbital in the heavier homologue is better accessible due to the higher energy whereas the lighter atoms easily engage in s/p hybridization because the radii of the $2s$ and $2p$ orbitals are similar to each other.

4. Conclusion

The calculated equilibrium structures of the $Mo(CO)_4$ complexes with *N*-heterocyclic carbene and analogues $[Mo(CO)_4\{NHE_{Me}\}]$ (**Mo4-NHE_{Me}**) show that the slighter complexes **Mo4-NHE_{Me}** possess end-on-bonded NHE_{Me} ligands when $E = C, Si, Ge$ with the bending angles, α , are 180° whereas the heavier adducts **Mo4-NH_{Sn}Me** and **Mo4-NHPb_{Me}** exhibit strongly side-on-bonded ligands which the bending angle, α become more acute. The lightest adduct **Mo4-NHC_{Me}** has a trigonal bipyramidal coordination mode where the ligand NHC_{Me} occupies an equatorial position. In contrast, the heavier species from **Mo4-NHSi_{Me}** to **Mo4-NHPb_{Me}** possess a

square pyramidal structure where the ligands from $NHSi_{Me}$ to $NHPb_{Me}$ occupy a basal position. The trend of the bond dissociations energies for the Mo-E bonds is **Mo4-NHC_{Me}** > **Mo4-NHSi_{Me}** > **Mo4-NHGe_{Me}** > **Mo4-NH_{Sn}Me** > **Mo4-NHPb_{Me}**. The theoretical data presented here clearly show that the bonding situation and molecular orbitals in **Mo4-NHE_{Me}** can be interpreted in terms of donor-acceptor interactions with NHE_{Me} ligands are very strong electron donors. The Mo-E bonds have a significant contribution from $(CO)_4Mo \leftarrow NHE_{Me}$ π -donation. Dispersion interactions have an influence on the calculated bond dissociation energies which show that the effect of bulky ligands may obscure the intrinsic Mo-E bond strength in **Mo4-NHC_{Me}**. The first detailed preparation of theoretical calculations for compounds $[Mo(CO)_4\{NHE_{Me}\}]$ will pose a challenge for the skills of synthetic chemists.

5. References

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