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-NH₄Me (called tetraylenes) with E = C, Si, Ge, Sn, Pb. The equilibrium structures of complexes [Mo(CO)₄·NHE₄Me] (Mo₄-NHE₄Me) exhibit an interesting trend which the lightest adduct Mo₄-NHC₄Me has a trigonal bipyramidal coordination mode where the ligand NHC₄Me occupies an equatorial position. In contrast, the heavier species from Mo₄-NHSi₄Me to Mo₄-NHPb₄Me possess a square pyramidal structure where the ligands from NH₅Si₄Me to NH₅Pb₄Me occupy a basal position. The lighter complexes Mo₄-NHE₄Me possess end-on-bonded NH₄Me ligands when E = C, Si, Ge with the bonding angles, α, are 180° whereas the heavier adducts Mo₄-NHSi₄Me and Mo₄-NHPb₄Me exhibit strongly side-on-bonded ligands which the bonding angle, α, become more acute. The trend of the bond dissociations energies-Dₑ [kcal/mol] (BDEs) for the Mo-E bonds is Mo₄-NHC₄Met > Mo₄-NHSi₄Me > Mo₄-NHG₄Me > Mo₄-NH₅Me > Mo₄-NHPb₄Me. Bonding analysis shows that the Mo-E bonds have a significant contribution from (CO)₄Mo ← NH₄Me-π-donation. This is because the energy levels of the π-type donor orbitals of Mo₄-NHC₄Me, Mo₄-NHSi₄Me, Mo₄-NHPb₄Me are higher lying than the σ-type donor orbitals. The NH₄Me ligands in Mo₄-NHE₄Me 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 điện tử kết hợp entender the gradient (BP86) từ các bộ hàm cơ sở khác nhau (SVP, TZVPP) được thực hiện cho việc tính toán lý thuyết của phức giả Mo(CO)₄ và phối tử N-heterocyclic carbene và các phức tương tự NH₄Me (gọi là tetraylenes) với E = C, Si, Ge, Sn, Pb. Cấu trúc của phức [Mo(CO)₄·NHE₄Me] (Mo₄-NHE₄Me) thể hiện sự khác biệt khả thi với Mo₄-NHC₄Me, trong đó Mo₄-NHC₄Me có cấu trúc phối tử tương tự NHC₄Me, chiếm vị trí trung tâm. Phức Mo₄-NHSi₄Me, Mo₄-NHPb₄Me không có cấu trúc phối tử tương tự với NH₄Me, chiếm vị trí trung tâm (basal – cạnh hướng cộng với bond). Các cấu trúc của phức Mo₄-NHE₄Me cho thấy các phức tương tự NH₄Me với E = C–Ge tạo thành phân tử Mo(CO)₄ một góc thẳng α = 180.0°, ngược lại, các phức nặng hơn Mo₄-NHE₄Me...
1. Introduction

Quantum chemical calculations of the unknown carbocarbene C(NHC)₂ with NHC is N-heterocyclic carbene which possess an unusual C ← C donor-acceptor bond of a divalent carbon(II) atom can acts as a 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 NHC 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 Mo⁴⁺ (Mo(IV)) and Mo⁶⁺ (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 NHE₆ ligands where E = C – Pb, which may exist, but have not yet been synthesized.

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 chemical behavior. Herein, we report on quantum chemical calculations using density functional theory (DFT-BP86) to investigate Mo₄-NHE₆ complexes and fragments which are shown in Scheme 1. The electronic structure of the molecules was analyzed with charge methods. The first detailed preparation of [(CO)₄Mo{NHE₆}] 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 Dᵣ is one measure of the strength in a chemical bond. For instance, the bond dissociation energy, Dᵣ [kcal/mol], for a bond (CO)₄Mo–NHE₆ which is broken through the reaction: [Mo(CO)₄–{NHE₆}] → (CO)₄Mo + NHE₆ of a molecule [Mo(CO)₄–NHE₆] and formed from the two fragments E₀[(CO)₄Mo] and E₀[NHE₆], is given by:

$$\Delta E = E[(CO)₄Mo] - E[(CO)₄Mo] - E[NHE₆] = Dᵣ.$$ 

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].

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**Scheme 1. Schematic representation of:** a) complexes Mo₄-NHE₆ and b) ligands NHE₆ with E = C – Pb

Those motivate us to choose [(CO)₄Mo-4{NHE₆}] (Mo₄-NHE₆) complexes to study in order to see whether the interesting bonding situation between Mo(CO)₄ and N-heterocyclic carbone-analogues, which is revealed by the bonding analysis has any unusual bonding mode to their...
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-TZVP 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 $[\text{Mo(CO)}_2\text{NHE}_{\text{Me}}]$, (Mo4-NHEMe) and free ligands NHEMe 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-NHCMc to Mo4-NHPbMe. The calculated Mo-NHCMc bond length of Mo4-NHCMc gives the shortest value (2.244 Å) and increases from Mo4-NHCMc to Mo4-NHPbMe (2.974 Å). This can be easily explained by the increasing radii of the group-14 atoms and the Mo(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-NHCMc, Mo4-NHSMc, and Mo4-NHGeMe have the NHCMc ligands bonded in a head-on way to the tungsten atom which bonding angles, $\alpha$, is 180.0°. In the structures of Mo4-NHSMc, the NHSMc ligands are bonded in a side-on manner with the bonding angles is 145.2°. The strongest side-on-bonded ligand when E = Pb has a bonding angle, $\alpha$, of 99.5°. The lightest adduct Mo4-NHCMe has a

![Figure 1. Optimized geometries of the complexes Mo4 – NHEMe 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 (CO)4Mo – NHEMe bonds in kcal/mol. The bending angle, $\alpha$, is the angle Mo-E-X where X is the midpoint between the N-N distance:](image1)

![Figure 2. Optimized geometries of the fragment NHEMe at the BP86/def2-SVP level. Bond lengths are given in Å; angles in degrees](image2)

trigonal bipyramidal coordination mode where the ligand NHCMc occupies an equatorial position. In contrast, the heavier species from Mo4-NHSMc to Mo4-NHPbMe possess a square pyramidal structure where the ligands from NHSMc to NHPbMe occupy a basal position. Figure 1 and Figure 2 also show that the E-N bonds of the free NHEMe ligands becomes slightly longer in the complexes Mo4-NHEMe where E = C, Si, Ge, and Sn while they become longer in the strongest side-on-bonded complex Mo4-NHPSbMe. Figure 1 gives the theoretical predicted BDEs for the Mo-E bonds of Mo4-NHCMc to Mo4-NHPbMe. There is a significantly decrease from the carbone complex Mo4-NHCMe ($D_e = 48.9$ kcal/mol) to the silylene Mo4-NHSMc 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 NHCMe ligand in Mo4-NHCMe is the strongest bonded while the heavier complexes Mo4-NHISMe to Mo4-NHPDPMe have weaker bonds [12, 13].

Table 1. Calculated bond dissociation energies De [kcal/mol] with and without corrections for dispersion interactions for the complexes Mo4-NHMe

| Compound          | BP86/TZVPP -D3 | BP86/TZVPP -D3 | ΔE  |
|-------------------|----------------|----------------|-----|
| Mo4–NHCMe         | 48.9           | 60.2           | 11.3|
| Mo4–NHIsMe        | 39.2           | 49.1           | 9.9 |
| Mo4–NHGeMe        | 31.8           | 40.7           | 8.9 |
| Mo4–NHGeSeMe      | 25.4           | 33.7           | 8.3 |
| Mo4–NHPDPMe       | 22.5           | 34.0           | 11.4|

Table 1 shows the theoretical BDEs with and without dispersion interactions for the complexes Mo4-NHMe 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 Mo4-NHPDPMe becomes uniformly larger by 11.4 kcal/mol when dispersion interaction is considered; this is because of the strongest side-on bonded ligand NHPDPMe. A significantly larger value is calculated for carbone complex Mo4–NHCMe (ΔE = 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 CH3 groups of free ligands and Mo(CO)4 fragment. In contrast to this, the calculated BDEs for the complexes Mo4-NHMe becomes uniformly smaller when E become heavier: i) The rather constant values for Mo4–NHGeMe and Mo4–NHGeSeMe (ΔE = 8.9 and 8.3 kcal/mol) except for the slightly larger BDE value (ΔE = 9.9 kcal/mol) in Mo4–NHGeSeMe which are shown by the longer bonds Mo-E compared with Mo-C bond in for Mo4–NHCMe adduct; ii) The complex Mo4–NHGeSnMe does not bring the large BDE value when dispersion correction is considered due to the slightly side-on-bonded ligand NHGeSnMe. 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 Mo4–NHCMe; and iv) The heavier atom with the Mo-Pb longest bond in the strongest side-on-bonded ligand of Mo4–NHPDPMe. Thus, although the calculated BDEs of Mo4–NHMe with the inclusion of dispersion interaction do not agree with the conclusion that the Mo-E bonds of the ligands NHMe 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

The bonding situation in compounds Mo4-NHEMe was analyzed using natural bond orbital (NBO) analysis. Table 2 gives results of the NBO calculations for parent compounds Mo4-NHMe – Mo4-NHPDPMe and for free ligands NHMe – NHPDPMe. The calculated partial charges show that the Mo(CO)4 fragment in the complexes always carries a negative charge, which slightly increases from Mo4–NHCMe (-0.47 e) to Mo4–NHPDPMe (-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 Mo4–NHCMe is much smaller (0.72) than that in heavier homologues where the values are almost constant between 0.90 for Mo4–NHISMe and 0.84 for Mo4–NHGeMe. The smallest value is given for the Mo4–NHPDPMe (0.50) and stays nearly the same in Mo4–NHGeSnMe (0.73) compared with the Mo-C bond in complex Mo4–NHCMe. Note that the bond order for the E-N bond becomes significantly smaller in the complexes Mo4–NHCMe – Mo4–NHPDPMe than in the free ligands NHMe – NHPDPMe. Table 2 also gives the atomic partial charges of the donor atoms E and the acceptor atom Mo in the complexes Mo4–NHMe. The molybdenum atom always carries a large negative charge between -1.40 e (E = C) and -1.68 e (E = Si). The donor atom has a positive charge of 0.30 e in Mo4–NHCMe 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 Mo4–NHCMe 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 [Mo ← E for the head-on-bonded lighter homologues to metal donation [Mo] → E for the side-on-bonded species in complexes. The NBO analysis at least suggests that the π-type acceptors is strong σ-donors and weak π-acceptors. This is possible for the ligands NHMe 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 Mo4–NHMe concerns the strength of the π donation (CO)4Mo ← NHMe which may be expected from the π lone-pair orbital of the ligands NHMe into the second vacant coordination side of Mo(CO)4. Since the molecules have C1 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° 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.

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 Mo4–NHCMe – Mo4–NHPDPMe and fragments. The partial charges, q, are given in electrons [e]

| Molecule   | Bond  | WBI | q[Mo(CO)4] | Atom | q (NPA) |
|------------|-------|-----|------------|------|---------|
| Mo4–NHCMe  | Mo – C| 0.72| -0.47      | Mo   | -1.40   |
The energy levels of the donor orbitals at the BP86/TZVPP level. Orbital energies are given in eV. The bonding situation gives the W → Mo and NHE → E donation. Although the ligands NHE are higher lying than the σ-type donor orbitals. From this, it follows that the shape of the MOs indicate that (CO)₃Mo ← NHE₄π donation is important in the complexes. The analysis of the bonding situation gives the W-E bonds have a significant contribution from (CO)₃Mo ← NHE₄ strong σ-donation and strong π-donation. This can be explained that the Mo(CO)₆ molecule is a 14-electron specie and lacks a 4-electron acceptor. Although the ligands NHE only retain one lone pair at E atom but the nitrogen in the NHE₄ ring can acts as ligands which indicate N → E donation and the NHE₄ ligands have the resonance form for molecules that can be realized because of the orbital overlap between the π-type lone pair and the N-E π*-orbitals which exhibits in more electron density at E atom. This makes the donor ligands NHE₄ can transfer more than one lone pair of electrons to the acceptor fragment Mo(CO)₆.

Figure 3 shows two occupied orbitals of the complexes which can be associated with (CO)₃Mo ← NHE₄σ 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–NHC₄–Mo₄–NH₄Pb are higher lying than the σ-type donor orbitals. From this, it follows that the shape of the MOs indicate that (CO)₃Mo ← NHE₄π donation is important in the complexes Mo₄–NHE₄. The analysis of the bonding situation gives the W-E bonds have a significant contribution from (CO)₃Mo ← NHE₄ strong σ-donation and strong π-donation. This can be explained that the Mo(CO)₆ molecule is a 14-electron specie and lacks a 4-electron acceptor. Although the ligands NHE only retain one lone pair at E atom but the nitrogen in the NHE₄ ring can acts as ligands which indicate N → E donation and the NHE₄ ligands have the resonance form for molecules that can be realized because of the orbital overlap between the π-type lone pair and the N-E π*-orbitals which exhibits in more electron density at E atom. This makes the donor ligands NHE₄ can transfer more than one lone pair of electrons to the acceptor fragment Mo(CO)₆.
The above results give 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 NHEMe. Figure 4 graphically shows the energy levels of the two highest lying occupied MOs which have σ or π symmetry of the ligands NHEMe. It is clear to show that, in NHEMe, the energy level of the σ orbital rises, whereas the π 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 NHEMe rationalize the preference of the heavier ligands for a side-on coordination to the Mo atom, where (CO)4Mo ← 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 NHEMe can be explained by various factors that also influence the bonding angles, α, of the ligands. The bonding 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{NHEMe}] (Mo4-NHEMe) show that the lighter complexes Mo4-NHEMe possess end-on-bonded NHEMe ligands when E = C, Si, Ge with the bonding angles, α, are 180° whereas the heavier addsucts Mo4-NHSSMe and Mo4-NHPbMe exhibit strongly side-on-bonded ligands which the bonding angle, α, become more acute. The lightest adduct Mo4-NHCMe has a trigonal bipyramidal coordination mode where the ligand NHCMe occupies an equatorial position. In contrast, the heavier species from Mo4-NHSSMe to Mo4-NHPbMe possess a square pyramidal structure where the ligands from NHSSMe to NHPbMe occupy a basal position. The trend of the bond dissociations energies for the Mo-E bonds is Mo4-NHCMe > Mo4-NHSSMe > Mo4-NHGeMe > Mo4-NHPSiMe > Mo4-NHPbMe. The theoretical data presented here clearly show that the bonding situation and molecular orbitals in Mo4-NHEMe can be interpreted in terms of donor-acceptor interactions with NHEMe ligands are very strong electron donors. The Mo-E bonds have a significant contribution from (CO)4Mo ← NHEMe 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-NHEMe. The first detailed preparation of theoretical calculations for compounds [Mo(CO)4{NHEMe}] will pose a challenge for the skills of synthetic chemists.

5. References

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