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Transition metal complexes of NHE ligands [(CO)$_4$W-{NHE}] with E = C – Pb as tracers in environmental study: structures, energies, and natural bond orbital of molecular interaction

Hợp chất của kim loại chuyển tiếp chứa phối tử NHE đóng vai trò là những hợp chất điển hình trong nghiên cứu môi trường [(CO)$_4$W-{NHE}] với E = C – Pb: Cấu trúc, năng lượng, và orbital liên kết tự nhiên của tương tác phân tử

Research article

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Quantum chemical calculations at BP86/TZVPP//BP86/SVP have been carried out for the N-heterocylic carbene and analogues complexes (tetrylene) [(CO)$_4$W-NHE] (W4-NHE) with E = C – Pb. The tetrylene complexes W4-NHE possess end-on-bonded NHE ligands (E = C, Si), while for E = Ge and Sn, they possess slightly side-on-bonded ligands. The strongest side-on-bonded ligand when E = Pb has a bending angle of 102.9°. The trend of the bond dissociations energies (BDEs) for the W-E bond is W4-NHC > W4-NHSi > W4-NHGe > W4-NHSn > W4-NHPb. Analysis of the bonding situation suggests that the NHE ligands in W4-NHE are strong σ-donors and weak π-donors. This is because the tetrylenes have only one lone-pair orbital available for donation. The polarization of the W-E bond and the hybridization at atom E explain the trend in the bond strength of the tetrylene complexes W4-NHE. The W-E bonds of the heavier systems W4-NHE are strongly polarized toward atom E giving rise to rather weak electrostatic attraction with the tungsten atom which is the main source for the decreasing trend of the bond energies. The theoretical calculations suggest that transition-metal complexes tetrylenes [(CO)$_4$W-{NHE}] (E = C – Pb) should be synthetically accessible compounds with tetrylenes NHE act as two-electron-donor ligands in complexes.

Phân tích cấu trúc và bản chất liên kết hóa học của hợp chất với kim loại chuyển tiếp chứa phối tử N-heterocyclic carbene và các đồng đẳng (tetrylene) [(CO)$_4$W–NHE] (W4-NHE) với E = C – Pb sử dụng tính toán hóa lượng tử ở mức BP86/TZVPP//BP86/SVP. Cấu trúc của phức W4-NHE cho thấy các phối tử NHE với E = C, Si tạo với phân tử W(CO)$_4$ một góc thẳng α = 180,0°, trong khi đó các phức W4-NHE thì phối tử NHE với E = Ge – Pb tạo liên kết với nhóm W(CO)$_4$ một góc cong α < 180,0° và góc cong càng trở nên nhọn hơn khi E = Pb (α = 102.9°). Năng lượng phân ly liên kết của liên kết W-E giảm dần: W4-NHC > W4-NHSi > W4-NHGe > W4-NHSn > W4-NHPb. Tính toán hóa lượng tử trong phức [(CO)$_4$W-{NHE}] (E = C – Pb) cho thấy phối tử tetrylene là chất cho electron. Điều này có thể do phối tử tetrylene chỉ giữ lại một cặp electron tại nguyên tử E để đóng vai trò là chất cho điện tử. Độ bền liên kết của phức W4-NHE được giải thích nhờ vào độ phân cực của liên kết W-E và sự lai hóa của nguyên tử trung tâm E. Nguyên nhân chính làm giảm dần năng lượng liên kết là do liên kết W-E của các phức nặng hơn W4-NHE bị phân cực mạnh về phía nguyên tử E dẫn đến lực hút tĩnh điện với nguyên tử W yếu dần. Hệ phức nghiên cứu được coi là hợp chất điển hình cho các nghiên cứu thực nghiệm.

Keywords: Tetrylene, bond disscosiation energy (BDE), end-on-bonded ligands, side-on-bonded ligands, transition metal complexes, natural bond orbital (NBO).

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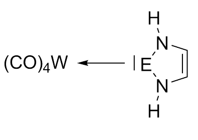
1. Introduction

As has been mentioned in the previous papers [13, 16], the recent revival of carbodiphosphorane (CDP) chemistry and the interpretation of $C(PR_3)_2$ as divalent carbon(0) compounds (carbones), in which the carbon atom retains two lone electron pairs, and is bonded to two σ-donor ligands L → C ← L [15, 21]. The first example for this bonding mode was proposed is the carbondiphosphorane $C(PPh_3)_2$, which was synthesized in 1961 [15], and structurally characterized by X-ray analysis in 1978 [5]. After realizing the particular bonding situation in CDPs [15, 20, 21], quantum chemical calculations of the hitherto unknown carbodicarbenes $C(NHC)_2$ (NHC=N-heterocyclic carbene) [20], which possess an unusual C → C donor-acceptor bond where a divalent carbon(II) atom acts as σ-donor and the divalent carbon(0) atom is a σ-acceptor, were performed. Carbodicarbenes were synthesized and structurally characterized by Bertrand et al [2], and also studied by Fürstner and co-workers [4]. A theoretical study on carbodicarbenes and related compounds [9] showed other divalent carbon(0) compounds, which had already been previously synthesized, but the donor-acceptor bonds had not been identified [18]. The carbenes, CR_2 possess only one lone-pair electron at carbon and have two electron-sharing bonds (C-R) to a carbon atom in the ^3P ground state [7, 10]. Striking experimental proof for the different donor behavior of carbenes and carbones has recently been reported by Alcarazo et al [6]. Moreover, it has been known that transition metal (TM) complexes with NHC ligands [7] and related systems [6], as well as those with heavier homologues NHE where E = Si – Pb have been extensively studied in the recent past [12]. This is because NHC ligands are excellent catalysts in various chemical reactions [22]. These findings suggest that it would be worth investigating the $W(CO)_4$ complexes of carbodicarbene analogues NHE where E = C – Pb, which may exist, but have not yet been synthesized. This paper provides detailed information on the structures and bonding situation of the tetrylene complexes $[(CO)_4W\text{-}\{NHE\}]$ (**W4-NHE**) (E = C – Pb). Although numerous theoretical studies of NHC complexes have been published [8], theoretical work on the heavier analogues is rather scarce [19]. To the best of our knowledge, the present work is the first detailed study of the structures and bonding situation of the complexes $[(CO)_4W\text{-}\{NHE\}]$. These investigated compounds are shown in Scheme 1:



E	Complex	Fragment
C	**W4-NHC**	NHC
Si	**W4-NHSi**	NHSi
Ge	**W4-NHGe**	NHGe
Sn	**W4-NHSn**	NHSn
Pb	**W4-NHPb**	NHPb

Scheme 1: Overview of the compounds investigated in this work and the numbering scheme used

The bond strengths of complexes **W4-NHE** and the fragments NHE were analyzed by calculating the geometries and BDEs. The W-E bonds in the complexes were calculated and interpreted in terms of partial charges. Furthermore, the differences and similarities in the bonding situation between the previously discussed tetrylene complexes $[(CO)_5W\text{-}\{NHE\}]$ [13] and the current systems $[(CO)_4W\text{-}\{NHE\}]$ (**W4-NHE**) are also investigated in this paper.

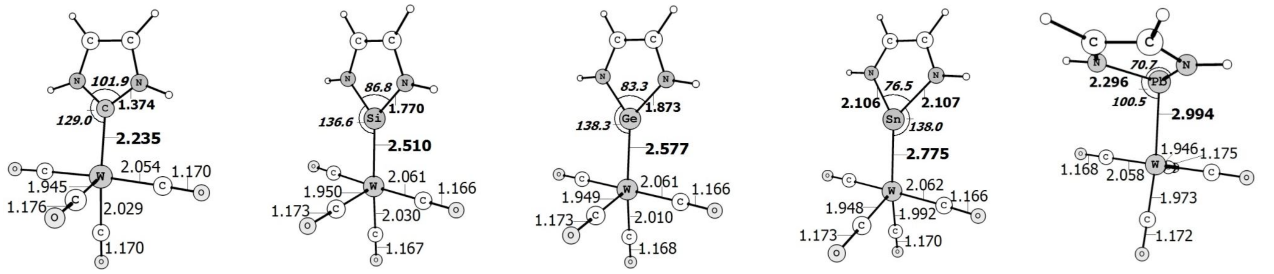
2. Computational methods

It has been given only a short summary of the computational part. Since the theoretical methods which were employed for this work are the same as in the previous papers [13, 20]. The geometries of the molecules were optimized without symmetry constraints using the Gaussian03 [3] optimizer together with Turbomole 6.1 [1] energies and gradients at the BP86 [14]/def2-SVP [17] level of theory (called BP86/SVP). Vibrational frequencies have also been calculated at the same level of theory to confirm that the structures are minima on the potential energy surface. For the heavier group-14 atoms Sn, Pb and for W, we used quasi-relativistic small-core effective core potentials (ECPs) [23]. The nature of the optimized geometries of all systems has been confirmed by vibrational frequency calculations. Wiberg bond orders and partial charges were calculated at BP86 with the larger basis sets def2-TZVPP [11] at the BP86/def2-SVP geometries using the NBO 3.1 program [24] link to Gaussian 03.

3. Results

3.1 Geometries and energies

The optimized geometries of compounds $[(CO)_4W\text{-}\{NHE\}]$ (**W4-NHE**) and the geometries of the free ligands NHC – NHPb are shown in Figure 1 and Figure 2 together with calculated values for the most important bond lengths and angles. Unlike the N-heterocyclic carbenes (NHCs) of $W(CO)_5$ complexes described by Nguyen and Frenking [13], all members of $[(CO)_4W\text{-}\{NHE\}]$ (E = C – Pb) are experimentally unknown. This present investigation is the first detailed study of **W4-NHE** complexes. The calculated W-NHC bond length of **W4-NHC** gives the shortest value (2.235 Å) and increases from **W4-NHC** to **W4-NHPb** (2.994 Å). This has essentially the same trend as that in previous systems $[(CO)_5W\text{-}\{NHE\}]$ [13] and is easily explained by the increasing radii of the group-14 atoms. Note that the W-NHE bond length of all species **W4-NHE** (E = C – Pb) is always slightly shorter than the bond length of $[(CO)_5W\text{-}\{NHE\}]$ complexes [13]. This might be caused by the lack of 2 electrons in these formal 16-electron systems, which is at least partly filled by the electron density in the p orbitals of NHC, NHSi, NHGe, and NHSn or the σ-lone-pair of NHPb.



W4 – NHC α = 179.5°; D_e = 56.1

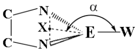
W4 – NHSi α = 178.8°; D_e = 44.5

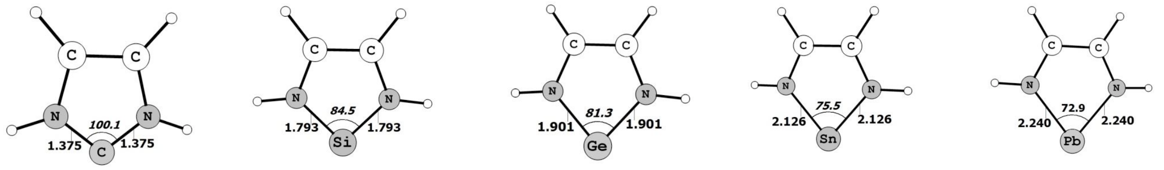
W4 – NHGe α = 177.0°; D_e = 35.7

W4 – NHSn α = 162.7°; D_e = 28.7

W4 – NHPb α = 102.9°; D_e = 24.1

Figure 1. Optimized geometries of the complexes W4-NHE 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)$_4$W-{NHE}] bonds in kcal/mol. The bending angle, α, is the angle W-E-X where X is the midpoint between the N-N distance:





NHC NHSi NHGe NHSn NHPb

Figure 2. Optimized geometries of the fragments NHE at the BP86/def2-SVP level. Bond lengths are given in Å; angles in degrees

The equilibrium structures of **W4-NHC** and **W4-NHSi** have the NHE ligands bonded in a head-on manner to the tungsten atom (bending angles, α, is approximately 180.0° (179.5°, 178.8°)). In the structure of **W4-NHGe** and **W4-NHSn**, the NHGe and NHSn ligands are bonded in a side-on manner, but the bending angles vary between 177.0 and 162.7°. Figure 2 shows that the plumbylene complex exhibits a significantly different bonding mode of the NHPb ligand compared with the other homologues. The strong side-on-bonded ligand when E = Pb has a bending angle, α, of 102.9°. Note that the E-N bonds of the free NHE ligands become slightly shorter in the head-on-bonded complexes **W4-NHE** where E = C, Si, Ge, and Sn while they become longer in the side-on-bonded complexes where E = Pb. Figure 1 also shows the calculated BDEs for the (CO)$_4$W-NHE bonds. It has been pointed out that the same calculated BDEs trend is observed for (CO)$_4$W-tetrylenes compared with (CO)$_5$W-tetrylenes as described previously [13]. There is a decrease from the carbene complex **W4-NHC** (D_e = 56.1 kcal/mol) to the lead compound **W4-NHPb** (D_e = 24.1 kcal/mol). The calculations suggest that the NHC ligand in **W4-NHC** is more strongly bonded than CO in W(CO)$_5$, while the heavier homologues **W4-NHE** where E = Si – Pb have weaker bonds. Comparison with the calculated BDEs values shows that the NHE ligand in **W4-NHC – W4-NHPb** is more strongly bonded than the NHE ligands in [(CO)$_5$W-{NHC}] – [(CO)$_5$W-{NHPb}] [13], since the W-NHE bond length is rather short in the **W4-NHC – W4-NHPb** complexes.

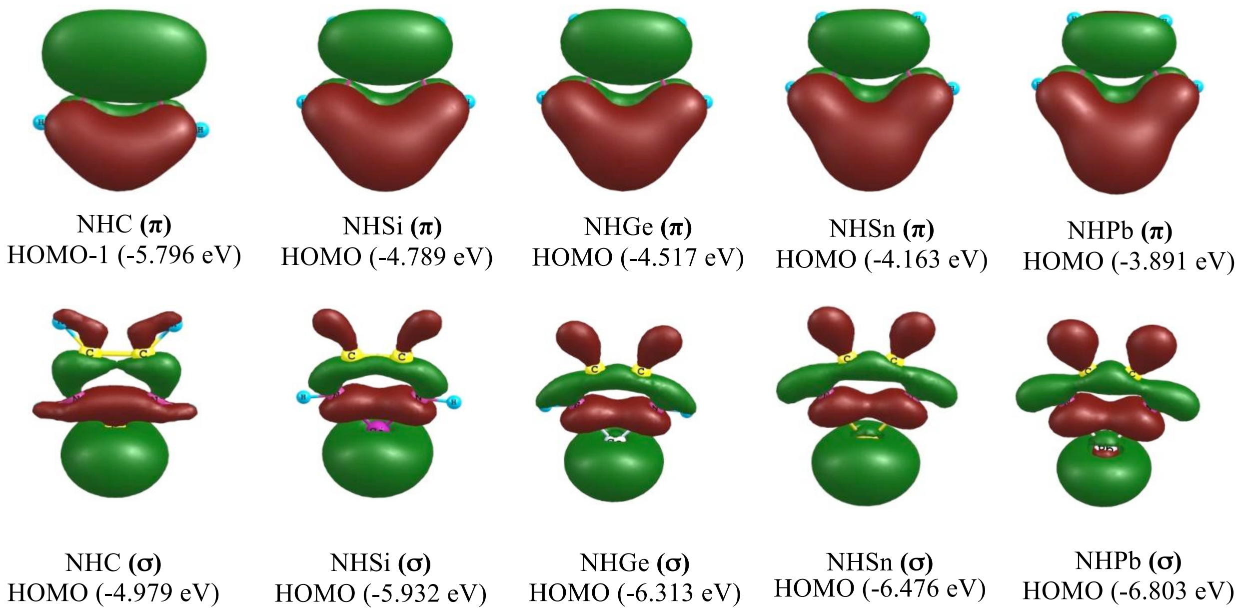
3.2 Natural Bond Orbital Analysis

Table 1 gives the results of calculations for the Wiberg bond orders and the partial charges in the compounds **W4-NHC – W4-NHPb** and free ligands NHC – NHPb which were calculated at the BP86/def2-TZVPP//BP86/def2-SVP level. The partial charge of the W(CO)$_4$ fragment is always negative. The calculated values increase from **W4-NHC** (-0.42 e) to **W4-NHSi** (-0.65 e) and they are nearly similar for **W4-NHGe** (-0.61 e) and **W4-NHSn** (-0.62 e), and become smaller for the plumbylene adduct **W4-NHPb** (-0.56 e). The atomic partial charges of the acceptor W atom carry negative charges between -1.00 e (E = C) and -1.39 e (E = Si). The carbon donor atom in **W4-NHC** has a small positive charge of 0.21 e and increases from the carbene complex to the silylene adduct **W4-NHSi** (1.36 e) and then remains almost constant for **W4-NHGe** (1.27 e) and **W4-NHSn** (1.26 e), and then it is 0.97 e for the plumbylene complex **W4-NHPb**. Note that the atomic partial charges of the donor atoms E in the free ligands NHC – NHPb become significantly smaller than those of complexes **W4-NHC – W4-NHPb**. The W-E bond order increases from **W4-NHC** (0.72) to **W4-NHSi** (0.92), but then decreases from **W4-NHGe** (0.86) to **W4-NHSn** (0.81) to **W4-NHPb** (0.51). Note that the bond order for the E-N bond becomes significantly smaller in the complexes **W4-NHC – W4-NHPb** compared with the free ligands NHC – NHPb. A comparison between the compounds **W5-NHC – W5-NHPb** which have been reported in the recent past [13] and the current compounds **W4-NHC – W4-NHPb** shows that the Wiberg bond orders and partial charges stay nearly the same trend in the complexes as those in the free ligands in two systems. The partial charges and bond orders in the **W4-NHE** complexes suggest that (i) the trend of the partial charges in **W4-NHE** do not support the suggestion that there is a change from ligand donation [W] ← NHE for the head-on-bonded lighter homologues to metal donation [W] → NHE for the side-on-bonded species, and (ii) the trend of the bond orders shows that neither the charge distribution nor the bond order correlate with the BDE of the tetrylene NHE ligands. In particular, the partial charges are also determined by the differences in the E-N bonds. From this it follows that neither the charge distribution nor the bond order correlate with the BDE of the tetrylene ligands NHE. The calculated equilibrium structures of the carbon complexes **W4-NHC** clearly possess end-on-bonded ligands and the heavier adducts of **W4-NHE** also exhibit slightly end-on-bonded NHE ligands when E = Si, Ge, and Sn. However, the heavier homologues **W4-NHPb** of the tetrylenes exhibit side-on-bonded NHE ligands, where the bending angles, α, become more acute when E becomes heavier. The trend of theoretically predicted for the BDEs which decrease from the lighter to the heavier tetrylenes. Bonding analysis suggests that the weaker bonds of the heavier tetrylene complexes [$(CO)_4W$-{NHE}] are caused by a significant decrease in the electrostatic component and orbital interaction of the W-E bonds. The fact is that, the W atom of $W(CO)_4$ needs 4 electrons to get 18 electrons in the metal complex; thus, the π-interactions in **W4-NHE** are due to weak π-donation, which is also irrelevant for the bond strength.

Table 1. NBO results at the BP86/def2-TZVPP//BP86/def2-SVP level for complexes W4-NHC – W4-NHPb and fragments NHE. The partial charges, *q*, are given in electrons [e]

Molecule	Bond	WBI	*q*[$W(CO)_4$]	Atom	*q*
W4-NHC	W-C	0.72	-0.42	W	-1.00
	$C-N_1$	1.28		C	0.21
	$C-N_2$	1.28		N	-0.47
NHC	$C-N_1$	1.31		C	0.04
	$C-N_2$	1.31		N	-0.53
	W-Si	0.92	-0.65	W	-1.39
W4-NHSi	$Si-N_1$	0.83		Si	1.36
	$Si-N_2$	0.83		N	-0.90
NHSi	$Si-N_1$	0.84		Si	0.84
	$Si-N_2$	0.84		N	-0.93
	W-Ge	0.86	-0.61	W	-1.34
W4-NHGe	$Ge-N_1$	0.79		Ge	1.27
	$Ge-N_2$	0.79		N	-0.87
NHGe	$Ge-N_1$	0.80		Ge	0.84
	$Ge-N_2$	0.80		N	-0.91
	W-Sn	0.81	-0.62	W	-1.33
W4-NHSn	$Sn-N_1$	0.71		Sn	1.26
	$Sn-N_2$	0.71		N	-0.86
NHSn	$Sn-N_1$	0.75		Sn	0.84
	$Sn-N_2$	0.75		N	-0.90
	W-Pb	0.51	-0.56	W	-1.13
W4-NHPb	$Pb-N_1$	0.59		Pb	0.97
	$Pb-N_2$	0.59		N	-0.76
NHPb	$Pb-N_1$	0.74		Pb	0.80
	$Pb-N_2$	0.74		N	-0.87

The above results have demonstrated that, although charge and energy decomposition analyses give insight into the nature of bonding, the trend of the bond strength and preference of the heavier ligands for side-on bonding in both systems have yet to be explained. A pivotal role for understanding the differences between the bonding of the ligands lies in the highest lying occupied MOs of the free ligands, which have been considered for **W4-NHE** system. The highest-lying occupied molecular orbitals (σ and π) of ligand NHE are shown in Figure 3. The energy level of the π orbital increases while 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 allow rationalization of the preference of the heavier ligands for coordination to the metal where the theoretically predicted bonding mode for current complexes **W4-NHE** is very similar to that of system [$(CO)_5W$-{NHE}] **(W5-NHE)** [13]. The end-on coordination of the lighter homologues NHC – NHSn can be explained by various factors that also influence the bending angle, α, of the ligands. Hybridization of the valence s and p donor orbitals of E atom was also investigated.


NHC **(π)** HOMO-1 (-5.796 eV)
NHSi **(π)** HOMO (-4.789 eV)
NHGe **(π)** HOMO (-4.517 eV)
NHSn **(π)** HOMO (-4.163 eV)
NHPb **(π)** HOMO (-3.891 eV)

NHC **(σ)** HOMO (-4.979 eV)
NHSi **(σ)** HOMO (-5.932 eV)
NHGe **(σ)** HOMO (-6.313 eV)
NHSn **(σ)** HOMO (-6.476 eV)
NHPb **(σ)** HOMO (-6.803 eV)

Figure 3. Graphical plot of the energetically highest lying σ and π orbitals of NHE (NHC – NHPb

It is pointed out that atoms of the first octal row easily engage in *s/p* hybridization because the radii and energies of the *2s* and *2p* orbitals are not very different from each other [13]. Polarization of the W-E σ-bonds given by the natural bond orbitals and hybridization of the W-E bonds at the E atom in the **W4-NHE** complexes are shown in Table 2. The W-C bond of **W4-NHC** complex is slightly more polarized (73.8% at C). Note that the trend of the polarization and hybridization values of the W-E bonds in the heavier tetrylene complexes **W4-NHSi – W4-NHPb** is similar to the trend of the tetrylene adducts [(CO)$_5$W-{NHE}] (**W5-NHSi – W5-NHPb**) [13]. The W-Si bond in **W4-NHSi** is less polarized (63.0% at Si) than the W-C bond in **W4-NHC** and become increasingly more polarized toward to atom E, which is 63.0% at atom Si and 88.9% at atom Pb. Table 2 also shows that the *%s* character at atom C is 46.1% for **W4-NHC** and then increases from **W4-NHSi** (53.2%) to **W4-NHPb** (57.0%).

Table 2. Polarization of the W-E σ-bond and hybridization of σ-donor orbital at atom E from NBO analysis of W4-NHE. The calculations were carried out at the BP86/TZVPP//BP86/SVP level

Complex	Polarization		Hybridization	
	%(W)	%(E)	% s (E)	% p (E)
W4-NHC	26.2	73.8	46.1	53.9
W4-NHSi	37.0	63.0	53.2	46.7
W4-NHGe	34.3	65.7	53.3	46.7
W4-NHSn	33.7	66.3	51.7	48.3
W4-NHPb	11.1	88.9	57.0	42.9

This indicates that the tetrylene adducts have only one σ-lone-pair orbital for the donor-acceptor interactions in the side-on-bonded complexes **W4-NHPb**. The trend toward stronger polarization of the W-E bonds explains why the electrostatic contribution to the bond strongly decreases for heavier atoms E.

3. Conclusion

The equilibrium geometries of the tetrylene complexes [(CO)$_4$W-{NHE}] (**W4-NHE**) possess end-on-bonded NHE ligands (E = C, Si), while for E = Ge and Sn they possess slightly side-on-bonded ligands. The strong side-on-bonded ligand when E = Pb has a bending angle of 102.9°. The trend of the calculated BDEs is **W4-NHC > W4-NHSi > W4-NHGe > W4-NHSn > W4-NHPb**. Thus, the donation of a second pair of electrons does not play a role to the trend in the dissociation energies. Analysis of the bonding situation suggests that the NHE ligands in **W4-NHE** are strong σ-donors and weak π-donors. Furthermore, the polarization of the W-E bond and hybridization at atom E also explains the trend in the bond strength of the tetrylene complexes **W4-NHE**. The hybridization of the donor orbital at atom E has the same *%s* character trend of hybridization compared with W(CO)$_5$-tetrylene complexes [13]. This can be explained by the fact that the tetrylenes have only one lone-pair orbital available for donation. In summary, quantum-chemical calculations suggest that transition-metal complexes tetrylenes [(CO)$_4$W-{NHE}] (E = C – Pb) are suitable target for synthesis and the theoretical calculations for compounds of this study not only give insight into the nature of the molecules investigated, but also open up new applications in environmental sciences.

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