A comparison for donor-acceptor interactions between E(PH$_3$)$_2$ and NHE$_{Me}$ ligands (E = C to Pb) of W(CO)$_5$ complexes using energy decomposition analysis method with natural orbitals for chemical valence theory

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Abstract

Quantum chemical calculations at the BP86/TZ2P+ level of theory are performed for a comparison of density functional theory (DFT) between tetrylones [(CO)$_5$W-{E(PH$_3$)$_2$}] (**W5-EP2**) and tetrylenes [(CO)$_5$W-{NHE$_{Me}$}] (**W5-NHE$_{Me}$**) when E = C to Pb. The EDA-NOCV results suggest that the W-E bond dissociation energies (BDEs) in tetrylone complexes increase from the lighter to the heavier homologues. The W-E bond dissociation energies (BDEs) trend in **W5-EP2** comes from the increase in (CO)$_5$W←E(PH$_3$)$_2$ donation and strong electrostatic attraction, and that the ligands E(PH$_3$)$_2$ (**EP2**) are strong σ-donors and very weak π-donors. The W-E BDEs trend in tetrylene complexes **W5-NHE$_{Me}$** is opposite to that of the **W5-EP2** complexes which decrease from the lighter to the heavier homologues. The NHE$_{Me}$ ligands are strong σ-donors and weak π-acceptors. NOCV pairs were used in a description of the chemical bond between the W(CO)$_5$ fragment and the ligands in the transition-metal complexes and the results indicated that the NOCV pairs lead to very valuable description of the bonding situation of the fragment-ligand bond in complexes.

Keywords. Density functional theory; Bond dissociation energies (BDEs); Energy decomposition analysis (EDA); Natural Orbitals for Chemical Valence (NOCV).

1. INTRODUCTION

The description of bonding in transition metal complexes in terms of synergic processes of the ligand → metal electron donation and the metal → ligand back-donation has much influenced the way of thinking about the properties of transition-metal-based systems [1]. The development of *ab initio* methods of quantum chemistry and in particular of density functional theory (DFT) has given rise to fast progress in the theoretical description of transition metal complexes thanks to the results obtained from high-quality computations [2]. Classification of ligands according to their donor-acceptor properties allows us to understand the electronic structure of metal complexes as well as to predict and to rationalize their chemical reactivity

[1,3-5]. Numerous theoretical methods and concepts were applied in a description of donor-acceptor properties, including the interaction-energy partitioning schemes and energy decomposition analysis (EDA) [5, 6] techniques based on molecular orbital energies. The EDA gives very well-defined energy terms for the chemical bonds in molecules [6]. One of the several useful schemes that link the concepts of bond-order, bond-orbitals, and charge rearrangement with the deformation density is the method based on natural orbitals for chemical valence (NOCV) [7]. The EDA-NOCV method [1, 2, 8-10] combines both charge (NOCV) and energy (EDA) partitioning schemes for decomposition of the deformation density which is associated with the bond formation, $\Delta\rho$, into different components of the chemical bonds.

It has been known that the studies concerned with tetrylones (carbones, silylones, germylones, stannylones, plumbylones) EL_2 possessing two lone pairs at E central atom (E = C to Pb) are increasingly interested [9, 11-14]. Comparison with tetrylones, the tetrylenes (ER_2) (carbenes, silylenes, germylenes, stannylenes, plumbylenes) possess only one electron lone pair at E central atom and have two electron-sharing bonds (ER) to E atom [9, 12, 15]. Moreover, the structures and bonding situation of a complex of tungsten pentacarbonyl $W(CO)_5$ with tetrylones-$[W(CO)_5-\{C(PPh_3)_2\}]$ and tetrylenes-$[W(CO)_5-\{(NHC_H)_2\}]$ were analyzed using DFT calculations by Nguyen and Frenking [9].

The main purpose of the present paper is to briefly review the application of the EDA-NOCV approach in a comparison for donor-acceptor interaction between the two typical ligands, carbodiphosphorane-analogues (tetrylones) $E(PH_3)_2$ and N-heterocyclic carbene-analogues (tetrylenes) NHE_{Me} in transition metal complexes. We consider a comparative investigation of the bonding situation of the complexes $[(CO)_5W-\{E(PH_3)_2\}]$ (**W5-EP2**) and $[(CO)_5W-\{NHE_{Me}\}]$ (**W5-NHE$_{Me}$**) with E = C to Pb (Scheme 1). The electronic structures are analyzed using the energy partitioning method. We want to draw a thorough picture of electronic structures and natural of chemical bonding of free ligands ($E(PH_3)_2$ and NHE_{Me}) as donor fragments bonded with $W(CO)_5$ as acceptor fragments, and then a picture of structures and properties of parent complexes of the main group and transition metal complexes that carry tetrylone and tetrylene ligands.

E	Complex	Fragment	
C	**W5-CP2**	**CP2**	
Si	**W5-SiP2**	**SiP2**	
Ge	**W5-GeP2**	**GeP2**	$(CO)_5W$ ⟸ E ⟨ PH₃ PH₃
Sn	**W5-SnP2**	**SnP2**	
Pb	**W5-PbP2**	**PbP2**	
C	**W5-NHC$_{Me}$**	**NHC$_{Me}$**	
Si	**W5-NHSi$_{Me}$**	**NHSi$_{Me}$**	
Ge	**W5-NHGe$_{Me}$**	**NHGe$_{Me}$**	$(CO)_5W$ ⟵ E ⟨N-CH₃ / N-CH₃⟩
Sn	**W5-NHSn$_{Me}$**	**NHSn$_{Me}$**	
Pb	**W5-NHPb$_{Me}$**	**NHPb$_{Me}$**	

Scheme 1: Overview of the complexes investigated in this work.

2. COMPUTATIONAL DETAILS

In the introduced EDA-NOCV [1, 2, 9, 10], the bond dissociation energy, D_e, of a molecule is divided into the instantaneous interaction energy ΔE_{int} and the preparation energy ΔE_{prep}. Bond-dissociation energy (BDE) is one measure of the strength of a chemical bond. For instance, the bond dissociation energy, D_e [kcal/mol], for a bond carbene/carbone−$W(CO)_5$ which is broken through the reaction: carbene/carbone−$W(CO)_5$ → carbene/carbone + $W(CO)_5$ of a molecule and formed from the two fragments $E^0_{carbone/carbene}$ and $E^0_{tungsten\ pentacarbonyl}$, is given by:

$$\Delta E = E_{carbene/carbone-tungsten\ pentacarbonyl} - E^0_{carbone/carbene} - E^0_{tungsten\ pentacarbonyl} = -D_e \qquad (1)$$

And $\qquad \Delta E\ (= -D_e) = \Delta E_{int} + \Delta E_{prep} \qquad (2)$

The preparation energy ΔE_{prep} is the energy required to promote the fragments A and B from their equilibrium geometries in the electronic ground state to the geometries and electronic reference state that they have in the molecule. The interaction energy ΔE_{int} can be further divided into three main components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \qquad (3)$$

where ΔE_{elstat} is the quasiclassical electrostatic interaction energy between the fragments, calculated by means of the frozen electron density distribution of the fragments in the geometry of the molecules. ΔE_{Pauli} refers to the repulsive interactions between the fragments, which are caused by two electrons with the same spin cannot occupy the same region in space and can be calculated by enforcing the Kohn–Sham determinant on the superimposed fragments to obey the Pauli principle by anti-symmetrisation and renormalisation. The stabilising orbital interaction term ΔE_{orb} is calculated in the final step of the energy partitioning analysis when the Kohn–Sham orbitals relax to their optimal forms.

The EDA-NOCV method combines charge (NOCV) and energy (EDA) partitioning schemes to decompose the deformation density which is associated with the bond formation, $\Delta\rho$, into different components of the chemical bond. Furthermore, the EDA-NOCV calculations also provide pair wise energy contributions for each pair or interacting orbitals to the total bond energy. NOCV (Natural Orbital for Chemical Valence) [1, 2, 9] is defined as the eigenvector of the valence operator, ν, given by Equation (4):

$$\nu\,\psi_i = \upsilon\,\psi_i \qquad (4)$$

In the EDA-NOCV scheme the orbital interaction term, ΔE_{orb}, is given by equation 5:

$$\Delta E_{orb} = \sum_{k=1}^{N/2} \Delta E_k^{orb} = \sum_{k=1}^{N/2} \upsilon_k \left[-F_{-k,-k}^{TS} + F_{k,k}^{TS}\right] \quad (5)$$

in which $F^{TS}_{-k,-k}$ and $F^{TS}_{k,k}$ are diagonal transition-state Kohn–Sham matrix elements corresponding to NOCVs with the eigenvalues $-\upsilon_k$ and υ_k, respectively. The ΔE_k^{orb} term of a particular type of bond are assigned by visual inspection of the shape of the deformation density, $\Delta\rho_k$. The EDA-NOCV

scheme thus provides information about the strength of orbital interactions in terms of both, charge ($\Delta\rho_{orb}$) and energy contributions (ΔE_{orb}) in chemical bonds, even in molecules without symmetry.

In this work, the parent complexes (**W5-EP2**; **W5-NHE$_{Me}$**) and free ligands (**EP2**; **NHE$_{Me}$**) were optimized for the energy decomposition analysis with the program package ADF 2013.01 [16] with BP86 in conjunction with a triple-zeta-quality basis set using un-contracted Slater-type orbitals (STOs) augmented by two sets of polarization function with a frozen-core approximation for the core electrons [17]. An auxiliary set of *s*, *p*, *d*, *f*, and *g* STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle [18]. Scalar relativistic effects have been incorporated by applying the zeroth-order regular approximation (ZORA) [19]. The nature of the W-E bonds in **W5-EP2** and **W5-NHE$_{Me}$** were investigated at BP86/TZ2P+ using the EDA-NOCV method [1, 2, 12-15, 20] combines the energy decomposition analysis (EDA) [21] with the natural orbitals for chemical valence (NOCV) [2,20] under C1 symmetric geometries.

3. RESULTS AND DISCUSSION

The EDA-NOCV calculations give a thorough insight into the natural of the metal-ligand bonding in [(CO)$_5$W-{E(PH$_3$)$_2$}] (**W5-EP2**) and [(CO)$_5$W-{NHE$_{Me}$}] (**W5-NHE$_{Me}$**). This leads to a donor-acceptor description of the W-E bond in the two systems. Both **W5-EP2** and **W5-NHE$_{Me}$** molecules are divided into the fragments E(PH$_3$)$_2$; NHE$_{Me}$ and W(CO)$_5$ which are in the singlet state. There are no experimental results available for complexes [(CO)$_5$W-{E(PH$_3$)$_2$}] (**W5-EP2**) and [(CO)$_5$W-{NHE$_{Me}$}] (**W5-NHE$_{Me}$**). Note that the transition metal complexes W(CO)$_5$ that carry the more bulky tetrylone ligands as well as the less bulky tetrylene ligands have been recently described by Nguyen and Frenking [9]. This present work just focuses on the differences of the tetrylones and tetrylenes using the EDA scheme with the NOCV method. Firstly, the complexes **W5-EP2** are investigated which the numerical results of EDA-NOCV calculations are shown in Table 1. The EDA-NOCV results demonstrate that the increase in the metal-ligand bonding comes from the intrinsic interaction ΔE_{int} which rises from the lighter **W5-CP2** to the heavier homologues **W5-PbP2**. The preparation energies ΔE_{prep} change very little between 4.1 and 5.1 kcal/mol in **W5-SiP2** and **W5-PbP2**. The increase of the BDEs from the lighter to heavier adduct is determined by the intrinsic strength of the metal-

ligand bonds ΔE_{int}. The trend of the BDEs, D_e, for the W-E bond in the **W5-EP2** system is **W5-CP2** < **W5-SiP2** < **W5-GeP2** < **W5-SnP2** < **W5-PbP2**. The three main terms ΔE_{Pauli}, ΔE_{elstat}, and ΔE_{orb} are considered to inspect their contribution to the intrinsic energy ΔE_{int} of the molecules. The Pauli repulsion ΔE_{Pauli} has the smallest value of 95.2 kcal/mol for **W5-CP2** and gets larger from E = C to E = Pb (131.4 kcal/mol). It follows that the increase in bond strength for the heavier homologues in **W5-EP2** comes from stronger attraction rather than weaker repulsion [9]. Moreover, the electrostatic term ΔE_{elstat} continuously increases from **W5-CP2** (-94.9 kcal/mol) to the heavier complexes **W5-GeP2** (-107.3 kcal/mol), **W5-SnP2** (-118.5 kcal/mol) and it gives the strongest value in the lead complex **W5-PbP2** (-120.3 kcal/mol). The same trend is shown for the orbital interactions that the increase in the orbital interactions from **W5-CP2** (-47.4 kcal/mol) to **W5-PbP2** (-70.8 kcal/mol) while the percentage contribution of the orbital interactions gives 33.3% in **W5-CP2** and stays nearly the same from **W5-SiP2** (37.7%) to **W5-PbP2** (37.0%). The value of ΔE_{orb} comes mainly from σ- and π-contributions. The increase in bond strength in **W5-EP2** correlates with the decrease of ΔE_{elstat} and ΔE_{orb}. The increase in the attractive interaction ΔE_{elstat} and ΔE_{orb} of the heavier tetrylone ligands can be traced back to the σ-lone-pair orbital, which leads to stronger σ-orbital interaction ΔE_{orb} and electrostatic attraction ΔE_{elstat}. The σ-orbital contribution ΔE_{orb} is much stronger for the heavier complexes which means they increase from **W5-CP2** (-34.4 kcal/mol) to **W5-PbP2** (-60.6 kcal/mol). In contract to this, the π-orbital contribution ΔE_{π} are much weaker than those of ΔE_{σ} and decrease for the heavier group-14 ligands in complexes.

The ΔE_{orb} term was examined of the EDA-NOCV results further in order to obtain more detailed information on the natural of the bonding in **W5-CP2** to **W5-PbP2**. The plots of the pairs of orbitals ψ_k/ψ_{-k} that yield the NOCVs providing the largest contributions to the σ- and π-orbital terms ΔE_{σ} and ΔE_{π} in **W5-EP2** (E = C, Si) and the associated deformation densities $\Delta\rho$ and stabilization energies are shown in figure 1. The shape of orbital pairs in **W5-CP2** exhibits the head-on mode between C(PH$_3$)$_2$ and W(CO)$_5$, whereas the heavier homologues E(PH$_3$)$_2$ bind to W(CO)$_5$ in **W5-EP2** (E = Si – Pb) in side-on modes. The homologues **W5-GeP2 – W5-PbP2** exhibit similar shapes to those of adduct **W5-SiP2** and therefore, they are not shown in figure 1. Note that the green/red colors in the

figures for ψ_k/ψ_{-k} indicate the sign of the orbitals, and the white/black colors in the deformation density $\Delta\rho$ designate charge depletion, and the black areas point to charge accumulation. The charge flow $\Delta\rho$ occurs in the direction from white to black. Figures 1 (a) and 1 (d) give the NOCV pairs of σ-orbitals for **W5-CP2** and **W5-SiP2**. The orbital pairs ψ_1/ψ_{-1} can be considered as the dominant sources for the σ-bonding of the **EP2** ligands in the two complexes. The shape of the orbital pairs clearly indicates that σ-orbital interactions take place between the donor orbital of **CP2** and **SiP2** ligands which are mainly localized at the carbon(0) or silicon(0) and the acceptor orbital of W(CO)$_5$. The contributions of the π-orbital stabilization ΔE_π in **W5-EP2** are small (Table 1). It has been pointed out that the ligand E(PH$_3$)$_2$ are double donor and therefore, there should be no significant contribution from (CO)$_5$W→E(PH$_3$)$_2$ π-backdonation [9,11]. Figures 1(b) and 1(c) show two NOCV pairs ψ_k/ψ_{-k} (k = 2, 3) that dominate the total stabilization ΔE_π in **W5-CP2**. The shape of the NOCV pairs ψ_2/ψ_{-2} and

ψ_3/ψ_{-3} and deformation densities $\Delta\rho_2$ and $\Delta\rho_3$, reveal that the associated energy stabilization comes mainly from the charge relaxation within the W(CO)$_5$ acceptor fragment ($\Delta\rho_2$ (ΔE = -3.9 kcal/mol); $\Delta\rho_3$ (ΔE = -3.03 kcal/mol)). It follows that donation of the carbone π lone pair to the W(CO)$_5$ is very weak. The charge flows, and the associated stabilization energies which are shown in Figures 1 (e) and 1 (f) of **W5-SiP2** exhibits a strange trend compared with the NOCV pairs ψ_2/ψ_{-2} and ψ_3/ψ_{-3} as π-type orbitals in **W5-CP2**. The charge flow $\Delta\rho_2$ can be assigned to (CO)$_5$W→Si(PH$_3$)$_2$ π-back-donation where the Si-P vacant anti-bonding orbital acts as an acceptor. In contrast to this, the shape of the charge flow $\Delta\rho_3$ indicates that the stabilization of -4.7 kcal/mol comes from the relaxation of the acceptor fragment W(CO)$_5$. The W-E BDEs trend in **W5-EP2** comes from the increase in (CO)$_5$W←E(PH$_3$)$_2$ donation and from strong electrostatic attraction, and that the ligands E(PH$_3$)$_2$ (**EP2**) are strong σ-donors and very weak π-donors.

Table 1: EDA-NOCV results at the BP86/TZ2P+ level for complexes **W5-CP2** to **W5-PbP2** using the moieties [W(CO)$_5$] and [E(PH$_3$)$_2$] as interacting fragments. The complexes are analyzed with C1 symmetry. Energy values in kcal/mol

Complex	**W5-CP2**	**W5-SiP2**	**W5-GeP2**	**W5-SnP2**	**W5-PbP2**
Fragment	W(CO)$_5$	W(CO)$_5$	W(CO)$_5$	W(CO)$_5$	W(CO)$_5$
	CP2	**SiP2**	**GeP2**	**SnP2**	**PbP2**
ΔE_{int}	-47.1	-53.3	-54.3	-58.3	-59.7
ΔE_{Pauli}	95.2	119.9	118.2	129.6	131.4
ΔE_{elstat}[a]	-94.9 (66.7 %)	-107.9 (62.3 %)	-107.3 (62.2 %)	-118.5 (63.1 %)	-120.3 (63.0 %)
ΔE_{orb}[a]	-47.4 (33.3 %)	-65.3 (37.7 %)	-65.2 (37.8 %)	-69.4 (36.9 %)	-70.8 (37.0 %)
ΔE_σ[b]	-34.4 (72.6 %)	-49.8 (76.3 %)	-52.8 (81.0 %)	-58.0 (83.6 %)	-60.6 (85.6 %)
ΔE_π[b]	-10.6 (22.4 %)	-13.8 (21.1 %)	-10.2 (15.6 %)	-8.3 (11.9 %)	-7.8 (11.0 %)
ΔE_{rest}[b]	-2.4 (5.0 %)	-1.7 (2.6 %)	-2.2 (3.4 %)	-3.1 (4.5 %)	-2.4 (3.4 %)
ΔE_{prep}	4.2	4.1	4.8	5.0	5.1
ΔE (= -D_e)	-42.9	-49.2	-49.5	-53.3	-54.6

[a] The values in parentheses are the percentage contributions to the total attractive interaction $\Delta E_{elstat} + \Delta E_{orb}$.
[b] The values in parentheses are the percentage contributions to the total orbital interaction ΔE_{orb}.

The EDA-NOCV results of tetrylenes [(CO)$_5$W-{NHE$_{Me}$}] (**W5-NHE$_{Me}$**) are completely different from the tetrylone complexes. Table 2 shows that EDA-NOCV results at the BP86/TZ2P+ level for complexes **W5-NHC$_{Me}$**–**W5-NHPb$_{Me}$** using the moieties [W(CO)$_5$] and [NHE$_{Me}$] as interacting

fragments. The W-E BDEs trend in **W5-NHE$_{Me}$** is opposite to that of the **W5-EP2** complexes which decrease from the lighter to the heavier homologues (**W5-NHC$_{Me}$**: -D_e = -52.0kcal/mol; **W5-NHPb$_{Me}$**: -D_e = -29.0 kcal/mol). The trend of the bond dissociations energies (BDEs) D_e for the W-E bond

in **W5-NHE$_{Me}$** system is **W5-NHC$_{Me}$ > W5-NHSi$_{Me}$ > W5-NHGe$_{Me}$ > W5-NHSn$_{Me}$ > W5-NHPb$_{Me}$**. The decrease of the BDEs from the lighter to heavier adduct is determined by the intrinsic strength of the metal-ligand bonds ΔE_{int}. The NOCV pairs of **W5-**

NHE$_{Me}$ are considered like the tetrylone complexes. The shape of the NOCV pairs ψ_1/ψ_{-1} and the deformation densities $\Delta\rho_1$ of **W5-NHC$_{Me}$** exhibit typical features for $(CO)_5W\leftarrow$ NHC$_{Me}$ σ-donation.
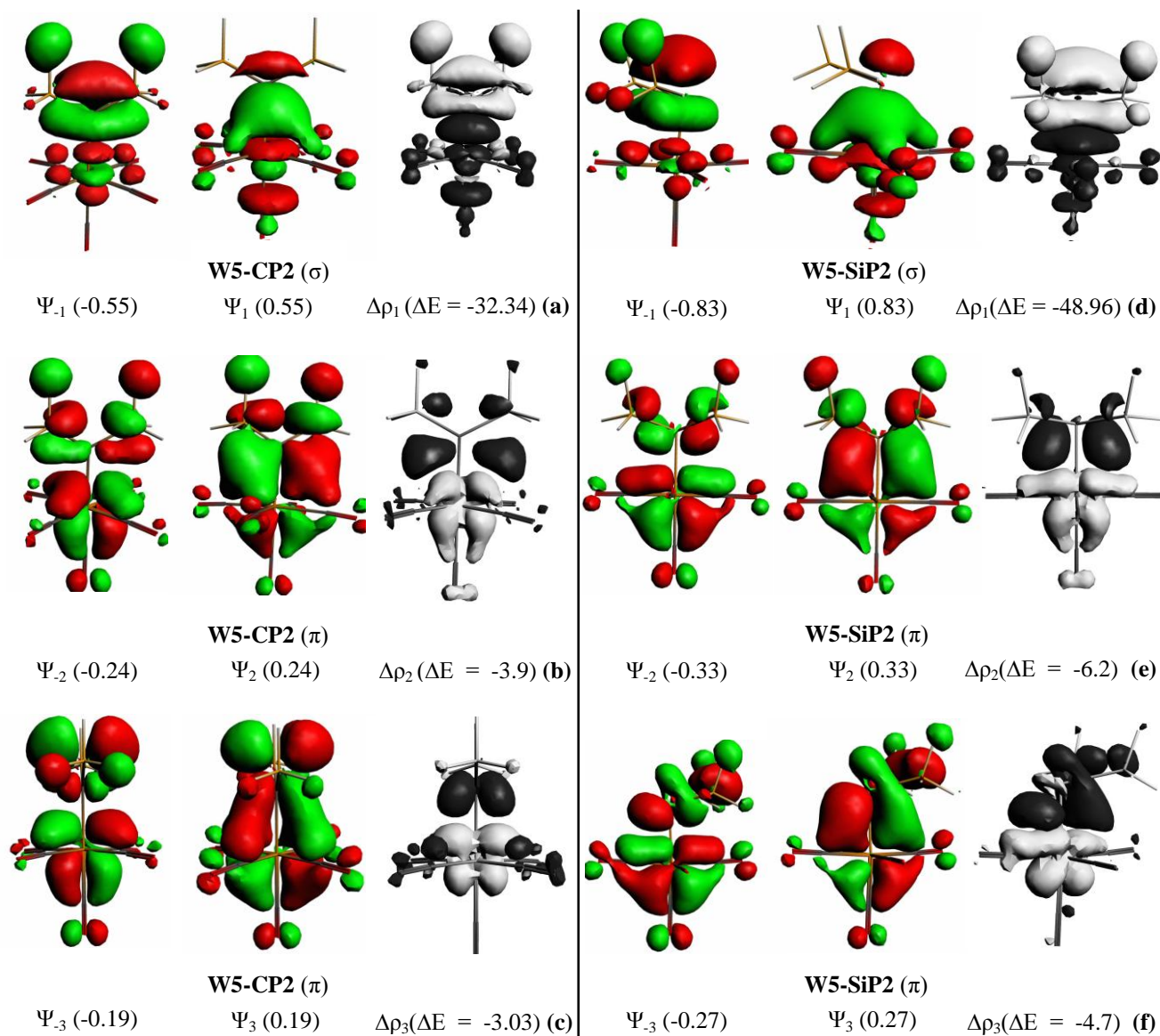

Fig. 1: Most important NOCV pairs of orbitals Ψ_{-k}, Ψ_k with their eigenvalues $-\upsilon_k$, υ_k given in parentheses, and the associated deformation densities $\Delta\rho_k$ and orbital stabilization energies ΔE (kcal/mol) for the complexes **W5-CP2** and **W5-SiP2**. The charge flow in the deformation densities is from the white →black region. (a) σ-NOCV of **W5-CP2**; (b) and (c) π-NOCVs of **W5-CP2**; (d) σ-NOCV of **W5-SiP2**; (e) and (f) π-NOCVs of **W5-SiP2**

Figure 2 (a) shows that the σ- type interaction is clearly from the donating NHC$_{Me}$ fragment to the accepting W(CO)$_5$ fragment. The shapes of the NOCV pairs ψ_2/ψ_{-2} and the deformation density $\Delta\rho_2$ in Figure 2 (b) show that stabilization of -7.1 kcal/mol can be assigned to $(CO)_5W\leftarrow$NHC$_{Me}$ π-donation while the stabilization of also comes from relaxation of the acceptor fragment W(CO)$_5$ in **W5-NHC$_{Me}$**. In contrast to this, the shapes of the NOCV pairs ψ_3/ψ_{-3} and particularly the deformation density $\Delta\rho_3$ in figure 2(c) clearly show that the small stabilization of -3.6 kcal/mol comes mainly from

relaxation of the acceptor fragment W(CO)$_5$. Figure 2-(d, e, f) shows significantly different EDA-NOCV results for **W5-NHPb$_{Me}$** because of the surprising structure of the plumbylene ligand, which is bonded through its π- electron density. Note that the structures and orbitals pairs of the lighter homologues **W5-NHE$_{Me}$** with E = C, Si, Ge have head-on modes between the ligands and W(CO)$_5$, whereas the heavier species **W5-NHSn$_{Me}$** and **W5-NHPb$_{Me}$** exhibit a side-on bonded ligands to the W(CO)$_5$ fragment. Figure 2 (d) shows that the σ-type interaction has the direction of the charge flow of (CO)$_5$W←NHPb$_{Me}$. The deformation density ψ_I exhibits an area of charge donation (white area) at the NHPb$_{Me}$ moiety associated with the deformation density $\Delta\rho_I$ and stabilization energy is 39.5 kcal/mol. Figures 2 (e) and 2 (f) show that the very weak π-type orbital interactions in **W5-NHPb$_{Me}$** come from typical π-back-donation (CO)$_5$W→ NHPb$_{Me}$ with the charge flow ψ_2/ψ_{-2} indicates stabilization of -2.4 kcal/mol and the

relaxation of the W(CO)$_5$ fragment with the charge flow ψ_3/ψ_{-3} indicates stabilization of -1.3 kcal/mol. Thus, the bonding in the tetrylene complexes **W5-NHE$_{Me}$** exhibits the typical feature in terms of strong σ-donation and weak π-donation. From the above results, it can be asserted that the weaker bonds of the heavier complexes [(CO)$_5$W-{NHE$_{Me}$}] result from a strong decrease in the electrostatic component of the W-E bonds. The π-interactions in [(CO)$_5$W-{NHE$_{Me}$}] are due to very weak π-backdonation and are also irrelevant for the bond strength. The decrease in the donation (CO)$_5$W ←NHE$_{Me}$, which is manifested in the calculated values for ΔE_σ and in the electrostatic attraction, ΔE_{elstat}, provides a rationale for the weaker bonding of the heavier atoms E. The differences between [(CO)$_5$W-{E(PH$_3$)$_2$}] (**W5-EP2**) and [(CO)$_5$W-{NHE$_{Me}$}] (**W5-NHE$_{Me}$**) can be mainly explained that the tetrylones-{E(PH$_3$)$_2$} have two lone pairs for donation while the tetrylenes NHE$_{Me}$ only retains one lone pair at central atom E.

Table 2: EDA-NOCV results at the BP86/TZ2P+ level for complexes **W5-NHC$_{Me}$** to **W5-NHPb$_{Me}$** using the moieties [W(CO)$_5$] and [NHE$_{Me}$] as interacting fragments. The complexes are analyzed with C1 symmetry. Energy values in kcal/mol

Complex	**W5-NHC$_{Me}$**	**W5-NHSi$_{Me}$**	**W5-NHGe$_{Me}$**	**W5-NHSn$_{Me}$**	**W5-NHPb$_{Me}$**
Fragment	W(CO)$_5$ NHC$_{Me}$	W(CO)$_5$ NHSi$_{Me}$	W(CO)$_5$ NHGe$_{Me}$	W(CO)$_5$ NHSn$_{Me}$	W(CO)$_5$ NHPb$_{Me}$
ΔE_{int}	-56.7	-48.2	-36.7	-32.1	-34.0
ΔE_{Pauli}	119.4	117.5	84.6	67.2	58.4
ΔE_{elstat}[a]	-123.3 (70 %)	-104.8 (63.3 %)	-72.2 (59.5 %)	-53.9 (54.3 %)	-46.0 (49.8 %)
ΔE_{orb}[a]	-52.8 (30 %)	-60.9 (36.7 %)	-49.1 (40.5 %)	-45.3 (45.7 %)	-46.3 (50.2 %)
ΔE_σ[b]	-36.3 (68.8 %)	-42.1 (69.1 %)	-35.0 (71.3 %)	-37.2 (82.1 %)	-41.1 (88.8 %)
ΔE_π[b]	-12.5 (23.7 %)	-12.8 (21.0 %)	-12.8 (26.1 %)	-7.1 (15.7 %)	-3.7 (8.0 %)
ΔE_{rest}[b]	4.0 (7.5 %)	-6.0 (9.9 %)	-1.3 (2.6 %)	-1.0 (2.2 %)	-1.5 (3.2 %)
ΔE_{prep}	4.7	2.9	2.3	2.0	5.0
ΔE (= - D_e)	-52.0	-45.3	-34.4	-30.1	-29.0

[a] The values in parentheses are the percentage contributions to the total attractive interaction $\Delta E_{elstat} + \Delta E_{orb}$.
[b] The values in parentheses are the percentage contributions to the total orbital interaction ΔE_{orb}.

4. CONCLUSION

The EDA scheme with the NOCV method has been combined for comparing the differences between W(CO)$_5$ complexes that carry E(PH$_3$)$_2$ and NHE$_{Me}$ ligands (E = C to Pb). The EDA-NOCV charge and energy decomposition scheme based on the Kohn-Sham approach not only makes it possible

to decompose the deformation density, $\Delta\rho$, into the different components of the chemical bond (σ, $\pi_\perp$, $\pi_\parallel$) of the chemical bond but also provides the corresponding energy contributions to the total bond energy. The EDA-NOCV results suggest that the W-E bond dissociation energies trend in **W5-EP2** comes from the increase in (CO)$_5$W←E(PH$_3$)$_2$ donation and from strong electrostatic attraction and

that the ligands $E(PH_3)_2$ are strong σ-donors and very weak π-donors. The W-E BDEs trend in **W5-NHE$_{Me}$** is opposite to that of the **W5-EP2** complexes which the NHE$_{Me}$ ligands are strong σ-donors and weak π-acceptors. The results show that the set of orbitals applied in the two fragments

in complexes allows for a separation and quantitative assessment of the contributions to the deformation density of donation from ligand → metal to back-donation ligand ← metal electron transfer processes.

W5-NHC$_{Me}$ (σ)

$Ψ_{-1}$ (-0.53) $Ψ_1$ (0.53) $Δρ_1(ΔE = -34.4)$ **(a)**

W5-NHC$_{Me}$ (π)

$Ψ_{-2}$ (-0.32) $Ψ_2$ (0.32) $Δρ_2(ΔE = -7.1)$ **(b)**

W5-NHC$_{Me}$ (π)

$Ψ_{-3}$ (-0.16) $Ψ_3$ (0.16) $Δρ_3(ΔE = -3.6)$ **(c)**

W5-NHPb$_{Me}$ (σ)

$Ψ_{-1}$ (-0.85) $Ψ_1$ (0.85) $Δρ_1(ΔE = -39.5)$ **(d)**

W5-NHPb$_{Me}$ (π)

$Ψ_{-2}$ (-0.24) $Ψ_2$ (0.24) $Δρ_2(ΔE = -2.4)$ **(e)**

W5-NHPb$_{Me}$ (π)

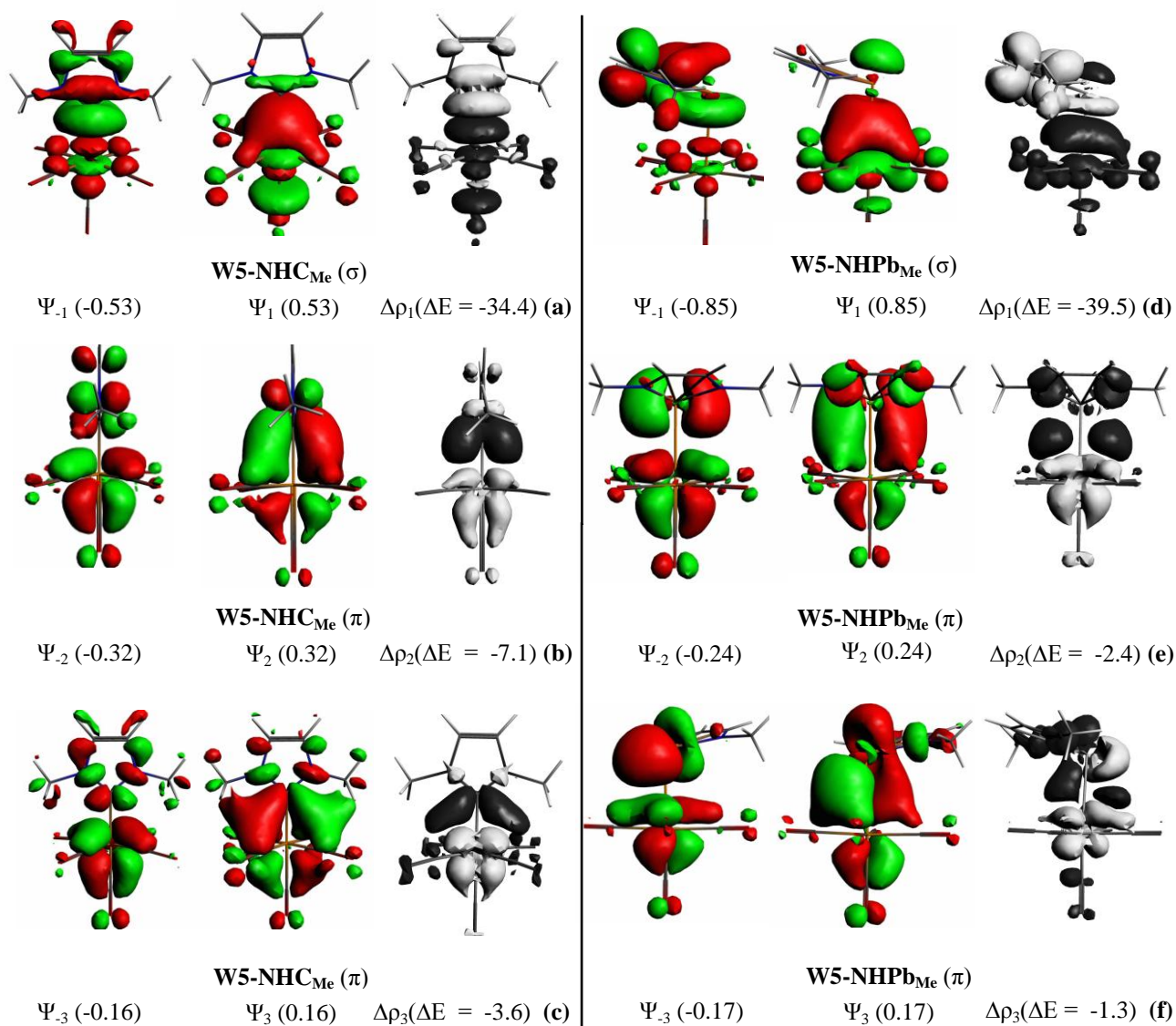$Ψ_{-3}$ (-0.17) $Ψ_3$ (0.17) $Δρ_3(ΔE = -1.3)$ **(f)**

Fig. 2: Most important NOCV pairs of orbitals $Ψ_{-k}$, $Ψ_k$ with their eigenvalues $-υ_k$, $υ_k$ given in parentheses, and the associated deformation densities $Δρ_k$ and orbital stabilization energies $ΔE$ for the complexes **W5-NHC$_{Me}$** and **W5-NHPb$_{Me}$**. The charge flow in the deformation densities is from the white → black region. (a) σ-NOCV of **W5-NHC$_{Me}$**; (b) and (c) π-NOCVs of **W5-NHC$_{Me}$**; (d) σ-NOCV of **W5-NHPb$_{Me}$**; (e) and (f) π-NOCVs of **W5-NHPb$_{Me}$**. Energy values in kcal/mol

REFERENCES

1. M. Mitoraj, A. Michalak. *Donor-Acceptor properties of Ligands from Natural Orbitals for Chemical Valence*, Organometallic, **26**, 6576-6580 (2007).

2. M. Mitoraj, A. Michalak. *Natural orbitals for chemical valence as description of chemical bonding in transition metal complexes*, J. Mol. Model, **13**, 347-355 (2007).

3. F. A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry,* Wiley, New York (1998).

4. F. P. Pruchnik, S. A. Duraj. *Organometallic Chemistry of the Transition Metal Elements*, Modern Inorganic Chemistry, New York, USA, (1990).

5. G. Frenking, N. Fröhlich. *Nature of the Bonding in Transition-Metal Compounds*, Chem. Rev., The. **100**, 717-774 (2000).

6. M. von Hopffgarten, G. Frenking. *Energy decomposition analysis*, Wires Comput. Mol. Sci, **2(1),** 43-62 (2012).

7. M. Mitoraj, A. Michalak, T. Ziegler. *Bond Orbitals from Chemical Valence Theory*, J. Phys. Chem. A, **112**, 1933-1939 (2008).

8. A. H. Pakiari, S. Fakhraee, S. M. Azami. *Decomposition of deformation density into orbital components*, Int. J. Quantum Chem., **108**, 415-422 (2008).

9. T. A. N. Nguyen, G. Frenking. *Transition-Metal Complexes of Tetrylones [(CO)$_5$W-E(PPh$_3$)$_2$] and Tetrylenes [(CO)$_5$W-NHE] (E=C–Pb): A Theoretical Study*, J. Chem. Eur., **18**, 12733-12748 (2012).

10. M. Lein, G. Frenking. *in Theory and Applications of Computational Chemistry* (Eds.: E. D. Clifford, G. Frenking, S. K. Kwang, E. S. Gustavo), Elsevier, Amsterdam (2005).

11. T. A. N. Nguyen, G. Frenking. *Structure and bonding of tetrylone complexes [(CO)$_4$W-E(PPh$_3$)$_2$]*

(E=C–Pb), Mol. Phys., **111**, 2040-2046 (2013).

12. T. A. N. Nguyen, T. P. L. Huynh, T. H. Dang. *Comparison for Bonding Situation between Tetrylone and Tetrylene Ligands of Tungsten Tetracarbonyl Complexes: A Theoretical Study*, Can. Chem. Trans, **4**, 143-156 (2016).

13. T. A. N. Nguyen, T.P. L. Huynh, T. H. Le, V. T. Pham, T. H. Dang. *Do Divalent Tetrylenes(II) Have a "Hidden" Divalent Tetrylones(0) Character in Borane Complexes? A Comparison of Donor-acceptor Interactions using Energy Decomposition Analysis Method with Natural Orbital for Chemical Valence Theory,* Smart Science, **4**, 28-37 (2016).

14. G. Frenking, M. Hermann, D. M. Andrada, N. Holzmann. *Donor–acceptor bonding in novel low-coordinated compounds of boron and group-14 atoms C–Sn*, Chem. Soc. Rev., **45**, 1129-1144 (2016).

15. T. A. N. Nguyen, el al. *Structural variations and chemical bonding in platinum complexes of Group 14 heavier tetrylene homologues (germylene to plumbylene),* IJC-A, **55A**, 269-276 (2016).

16. G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler. *Chemistry with ADF*, J. Comput. Chem., **22**, 931-967 (2001).

17. J. G. Snijders, P. Vernooijs, E. J. Baerends. *Roothaan-Hartree-Fock-Slater Atomic Wave Functions. Single-Zeta, Double-Zeta, and Extended Slater-Type Basis Sets for ^{87}Fr-^{103}Lr*, At. Data. Nucl. Data Tables, **26**, 483-437 (1981).

18. J. Krijn, E. J. Baerends. *Fit Functions in the HFS-Method,* Internal Report, Vrije Universiteit Amsterdam, The Netherlands (1984).

19. E. van Lenthe, A. Ehlers, Evert-Jan Baerends. *Geometry optimizations in the zero order regular approximation for relativistic effects*, J. Chem. Phys., **110**, 8943 (1999).

20. M. P. Mitoraj, A. Michalak, T. Ziegler. *A combined charge and energy decomposition scheme for bond analysis*, J. Chem. Theory Comput. 5, 962 (2009).

21. T. Ziegler, A. Rauk. *On the calculation of bonding energies by the Hartree Fock Slater method*, Theor. Chim. Acta, **46**, 1-10 (1977).

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