A comparison for donor-acceptor interactions between E(PH₃)₂ and NHE₅Me 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)₅W-{E(PH₃)₂}] (W₅EP₂) and tetrylones [(CO)₅W-{NHE₅Me}] (W₅NHE₅Me) 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 W₅EP₂ comes from the increase in (CO)₅W←E(PH₃)₂ donation and strong electrostatic attraction, and that the ligands E(PH₃)₂ (EP₂) are strong σ-donors and very weak π-donors. The W-E BDEs trend in tetrylone complexes W₅NHE₅Me is opposite to that of the W₅EP₂ complexes which decrease from the lighter to the heavier homologues. The NHE₅Me 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, Δρ, into different components of the chemical bonds.
It has been known that the studies concerned with tetrylones (carbones, silylones, germylones, stannylenes, plumblyenes) EL₂ possessing two lone pairs at E central atom (E = C to Pb) are increasingly interested [9, 11-14]. Comparison with tetrylones, the tetrylenes (ER₃) (carbones, silylones, germylones, stannylenes, plumblyenes) 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(PH₃)₂}] and tetrylenes-[W(CO)₅{NHC₆₁₂}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(PH₃)₂ and N-heterocyclic carbene-analogues (tetrylenes) NHE₆ₑ in transition metal complexes. We consider a comparative investigation of the bonding situation of the complexes [(CO)₅W{(E(PH₃))₂}] (W5-EP2) and [(CO)₅W{(NHE₆ₑ)}₂] (W5-NHE₆ₑ) 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(PH₃)₂ and NHE₆ₑ) 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.

<table>
<thead>
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</tr>
<tr>
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<tr>
<td>Si</td>
<td>W5-NHS₆ₑ</td>
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<tr>
<td>Ge</td>
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<td>Sn</td>
<td>W5-NHSnₑ</td>
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<tr>
<td>Pb</td>
<td>W5-NHPbₑ</td>
<td>NHPbₑ</td>
</tr>
</tbody>
</table>

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, Dₑ, of a molecule is divided into the instantaneous interaction energy ΔEₚₑ and the preparation energy ΔEₚₑ. Bond-dissociation energy (BDE) is one measure of the strength of a chemical bond. For instance, the bond dissociation energy, Dₑ [kcal/mol], for a bond carbene/carbene–W(CO)₅ which is broken through the reaction: carbene/carbene–W(CO)₅ → carbene/carbene + W(CO)₅ of a molecule and formed from the two fragments E⁰(carbene/carbene) and E⁰(tungsten pentacarbonyl), is given by:

\[
\Delta E = E_{\text{carbene/carbene–W(CO)₅}} - E_{\text{carbene/carbene–W(CO)₅}}^0
\]

And

\[
\Delta E = -Dₑ
\]

The preparation energy ΔEₚₑ 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 ΔEₚₑ can be further divided into three main components:

\[
\Delta E_{\text{int}} = \Delta E_{\text{elast}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}
\]

where ΔEₚₑ 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_{\text{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_{\text{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, Δρ, into different components of the chemical bond. Furthermore, the EDA-NOCV calculations also 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):

\[
\nu \psi_i = \nu \psi_i
\]

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

\[
\Delta E_{\text{orb}} = \sum_{k=1}^{N/2} \sum_{k'=1}^{N/2} \Delta e_{k,k'}^{\text{orb}} = \sum_{k=1}^{N/2} \sum_{k'=1}^{N/2} \left[ F_{k,k'}^{\text{TS}} - F_{k,k'}^{\text{K}} \right]
\]

in which F_{k,k'}^{\text{TS}} and F_{k,k'}^{\text{K}} are diagonal transition-state Kohn–Sham matrix elements corresponding to NOCVs with the eigenvalues −ν_k and ν_k, respectively. The ΔE_{\text{orb}} term of a particular type of bond are assigned by visual inspection of the shape of the deformation density, Δρ_k. The EDA-NOCV
scheme thus provides information about the strength of orbital interactions in terms of both, charge ($\Delta p_{orb}$) and energy contributions ($\Delta E_{orb}$) 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 CI symmetric geometries.

3. RESULTS AND DISCUSSION

The EDA-NOCV calculations give a thorough insight into the natural of the metal-ligand bonding in [(CO)$_3$W-E(PH$_3$)$_2$] (W5-EP2) and [(CO)$_3$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)$_3$, which are in the singlet state. There are no experimental results available for complexes [(CO)$_3$W-E(PH$_3$)$_2$] (W5-EP2) and [(CO)$_3$W-[NHE$_{Me}$]] (W5-NHE$_{Me}$). Note that the transition metal complexes W(CO)$_3$ that carry the more bulky tetrylene 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 tetrylenes 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 $\Delta E_{int}$ which rises from the lighter W5-CP2 to the heavier homologues W5-PbP2. The preparation energies $\Delta E_{prep}$ 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 $\Delta E_{int}$. 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 $\Delta E_{Pauli}$, $\Delta E_{elstat}$, and $\Delta E_{orb}$ are considered to inspect their contribution to the intrinsic energy $\Delta E_{int}$ of the molecules. The Pauli repulsion $\Delta E_{Pauli}$ 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 $\Delta E_{elstat}$ 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 $\Delta E_{orb}$ comes mainly from $\sigma$- and $\pi$-contributions. The increase in bond strength in W5-EP2 correlates with the decrease of $\Delta E_{elstat}$ and $\Delta E_{orb}$. The increase in the attractive interaction $\Delta E_{elstat}$ and $\Delta E_{orb}$ of the heavier tetrylene ligands can be traced back to the $\sigma$- lone-pair orbital, which leads to stronger $\sigma$-orbital interaction $\Delta E_{orb}$ and electrostatic attraction $\Delta E_{elstat}$. The $\pi$-orbital contribution $\Delta E_{\pi}$ 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 contrast to this, the $\pi$-orbital contribution $\Delta E_{\pi}$ are much weaker than those of $\Delta E_{\sigma}$ and decrease for the heavier group-14 ligands in complexes.

The $\Delta E_{orb}$ 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 $\psi_{\sigma}/\psi_{\pi}$ that yield the NOCVs providing the largest contributions to the $\sigma$- and $\pi$-orbital terms $\Delta E_{\sigma}$ and $\Delta E_{\pi}$ in W5-EP2 (E = C, Si) and the associated deformation densities $\Delta p$ 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)$_3$, whereas the heavier homologues E(PH$_3$)$_2$ bind to W(CO)$_3$ 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
The EDA-NOCV results of tetrylenes \((\text{CO})_3\text{W}^{[\text{NHE}_{Me}]}\) \((\text{W5-NHE}_{Me})\) are completely different from the tetrylone complexes. Table 2 shows that EDA-NOCV results at the BP86/TZ2P+ level for complexes \(\text{W5-NHC}_{Me}\)-\(\text{W5-NHPb}_{Me}\) using the moieties \([\text{W(CO)}_3]\) and \([\text{NHE}_{Me}]\) as interacting fragments. The W-E BDEs trend in \(\text{W5-NHC}_{Me}\) is opposite to that of the \(\text{W5-EP2}\) complexes which decrease from the lighter to the heavier homologues \((\text{W5-NHC}_{Me}: -D_c = -52.0\text{ kcal/mol}; \text{W5-NHPb}_{Me}: -D_c = -29.0\text{ kcal/mol})\). The trend of the bond dissociations energies (BDEs) \(D_c\) for the W-E bond

\[
\begin{align*}
\text{Complex} & \quad \text{W5-CP2} & \quad \text{W5-SiP2} & \quad \text{W5-GeP2} & \quad \text{W5-SnP2} & \quad \text{W5-PbP2} \\
\text{Fragment} & \quad \text{W(CO)}_3 & \quad \text{W(CO)}_3 & \quad \text{W(CO)}_3 & \quad \text{W(CO)}_3 & \quad \text{W(CO)}_3 \\
\Delta E_{\text{int}} & \quad -47.1 & \quad -53.3 & \quad -54.3 & \quad -58.3 & \quad -59.7 \\
\Delta E_{\text{Pauli}} & \quad 95.2 & \quad 119.9 & \quad 118.2 & \quad 129.6 & \quad 131.4 \\
\Delta E_{\text{elint}} & \quad -94.9 (66.7 \%) & \quad -107.9 (62.3 \%) & \quad -107.3 (62.2 \%) & \quad -118.5 (63.1 \%) & \quad -120.3 (63.0 \%) \\
\Delta E_{\text{orb}}[a] & \quad -47.4 (33.3 \%) & \quad -65.3 (37.7 \%) & \quad -65.2 (37.8 \%) & \quad -69.4 (36.9 \%) & \quad -70.8 (37.0 \%) \\
\Delta E_g[b] & \quad -34.7 (76.2 \%) & \quad -49.8 (76.3 \%) & \quad -52.8 (81.0 \%) & \quad -58.0 (83.6 \%) & \quad -60.6 (85.6 \%) \\
\Delta E_{\text{rest}}[b] & \quad -10.6 (22.4 \%) & \quad -13.8 (21.1 \%) & \quad -10.2 (15.6 \%) & \quad -8.3 (11.9 \%) & \quad -7.8 (11.0 \%) \\
\Delta E_{\text{acc}} & \quad -2.4 (5.0 \%) & \quad -1.7 (2.6 \%) & \quad -2.2 (3.4 \%) & \quad -3.1 (4.5 \%) & \quad -2.4 (3.4 \%) \\
\Delta E (=-D_c) & \quad -42.9 & \quad -49.2 & \quad -49.5 & \quad -53.3 & \quad -54.6 \\
\end{align*}
\]

[a] The values in parentheses are the percentage contributions to the total attractive interaction \(\Delta E_{\text{elint}} + \Delta E_{\text{orb}}\).

[b] The values in parentheses are the percentage contributions to the total orbital interaction \(\Delta E_{\text{orb}}\).
in W5-NHEMe system is W5-NHCMe > W5-NHSiMe > W5-NHGeMe > W5-NHSnMe > W5-NHPbMe. The decrease of the BDEs from the lighter to heavier adduct is determined by the intrinsic strength of the metal-ligand bonds $\Delta E_{int}$. The NOCV pairs of W5-NHEMe are considered like the tetrylone complexes. The shape of the NOCV pairs $\psi_1/\psi_2$ and the deformation densities $\Delta \rho_1$ of W5-NHCMe exhibit typical features for (CO)$_5$W$\leftarrow$NHCMe $\sigma$-donation.

**Fig. 1**: Most important NOCV pairs of orbitals $\Psi_i$, $\Psi_k$ with their eigenvalues $-\nu_i$, $\nu_k$ given in parentheses, and the associated deformation densities $\Delta \rho_i$ and orbital stabilization energies $\Delta E$ (kcal/mol) for the complexes W5-CP2 and W5-SiP2. The charge flow in the deformation densities is from the white $\rightarrow$ black region. (a) $\sigma$-NOCV of W5-CP2; (b) and (c) $\pi$-NOCVs of W5-CP2; (d) $\sigma$-NOCV of W5-SiP2; (e) and (f) $\pi$-NOCVs of W5-SiP2.

Figure 2 (a) shows that the $\sigma$-type interaction is clearly from the donating NHCMe fragment to the accepting W(CO)$_5$ fragment. The shapes of the NOCV pairs $\psi_2/\psi_3$ and the deformation density $\Delta \rho_2$ in Figure 2 (b) show that stabilization of -7.1 kcal/mol can be assigned to (CO)$_5$W$\leftarrow$NHCMe $\pi$-donation while the stabilization of also comes from relaxation of the acceptor fragment W(CO)$_5$ in W5-NHCMe. In contrast to this, the shapes of the NOCV pairs $\psi_3/\psi_4$ 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-NHPbMe 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-NHE₅Me with E = C, Si, Ge have head-on modes between the ligands and W(CO)₅, whereas the heavier species W₅-NHSiMe and W₅-NHPbMe 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←NHPbMe. The deformation density ρ/Δρ exhibits an area of charge donation (white area) at the NHPbMe moiety associated with the deformation density Δρ 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-NHPbMe come from typical π-back-donation (CO)₅→W←NHPbMe, with the charge flow ρ/Δρ indicates stabilization of -2.4 kcal/mol and the relaxation of the W(CO)₅ fragment with the charge flow (ρ/Δρ) indicates stabilization of -1.3 kcal/mol. Thus, the bonding in the tetrylene complexes W₅-NHE₅Me 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)₅W-{NHE₅Me}] result from a strong decrease in the electrostatic component of the W-E bonds. The π-interactions in [(CO)₅W-{NHE₅Me}] are due to very weak π-backdonation and are also irrelevant for the bond strength. The decrease in the donation (CO)₅→W←NHE₅Me, which is manifested in the calculated values for ΔEσ and in the electrostatic attraction, ΔEelstat, provides a rationale for the weaker bonding of the heavier atoms E. The differences between [(CO)₅W-{E(PH₃)₂}] (W₅-EP2) and [(CO)₅W-{NHE₅Me}] (W₅-NHE₅Me) can be mainly explained that the tetrylones-{E(PH₃)₂} have two lone pairs for donation while the tetrylenes NHE₅Me only retains one lone pair at central atom E.

Table 2: EDA-NOCV results at the BP86/TZ2P+ level for complexes W₅-NHCMe to W₅-NHPbMe using the moieties [W(CO)₅] and [NHE₅Me] as interacting fragments. The complexes are analyzed with C₁ symmetry.

<table>
<thead>
<tr>
<th>Complex</th>
<th>W(CO)₅</th>
<th>W(CO)₅</th>
<th>W(CO)₅</th>
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<th>W(CO)₅</th>
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<tbody>
<tr>
<td>Fragment</td>
<td>NHCMe</td>
<td>NHSiMe</td>
<td>NHGeMe</td>
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<td>ΔEint</td>
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<td>-36.7</td>
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<td>-34.0</td>
</tr>
<tr>
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<td>117.5</td>
<td>84.6</td>
<td>67.2</td>
<td>58.4</td>
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<td>-104.8 (63.3 %)</td>
<td>-72.2 (59.5 %)</td>
<td>-53.9 (54.3 %)</td>
<td>-46.0 (49.8 %)</td>
</tr>
<tr>
<td>ΔEorb[a]</td>
<td>-52.8 (30 %)</td>
<td>-60.9 (36.7 %)</td>
<td>-49.1 (40.5 %)</td>
<td>-45.3 (45.7 %)</td>
<td>-46.3 (50.2 %)</td>
</tr>
<tr>
<td>ΔEσ[b]</td>
<td>-36.3 (68.8 %)</td>
<td>-42.1 (69.1 %)</td>
<td>-35.0 (71.3 %)</td>
<td>-37.2 (82.1 %)</td>
<td>-41.1 (88.8 %)</td>
</tr>
<tr>
<td>ΔEπ[b]</td>
<td>-12.5 (23.7 %)</td>
<td>-12.8 (21.0 %)</td>
<td>-12.8 (26.1 %)</td>
<td>-7.1 (15.7 %)</td>
<td>-3.7 (8.0 %)</td>
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<tr>
<td>ΔErest[b]</td>
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</table>

[a] The values in parentheses are the percentage contributions to the total attractive interaction ΔEelstat + ΔEorb.
[b] The values in parentheses are the percentage contributions to the total orbital interaction ΔEorb.

4. CONCLUSION

The EDA scheme with the NOCV method has been combined for comparing the differences between W(CO)₅ complexes that carry E(PH₃)₂ and NHE₅Me 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, Δρ, into the different components of the chemical bond (σ, πₛ, πₕ) 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)₅W←E(PH₃)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 W$_5$-
NHE$_{Me}$ is opposite to that of the W$_5$-EP$_2$
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.

![Fig. 2: Most important NOCV pairs of orbitals $\Psi_k$, $\Psi_{k'}$ with their eigenvalues $\nu_k$, $\nu_{k'}$ given in parentheses, and the associated deformation densities $\Delta \rho_k$ and orbital stabilization energies $\Delta E$ for the complexes W$_5$-NHC$_{Me}$ and W$_5$-NHPb$_{Me}$. The charge flow in the deformation densities is from the white → black region.](image)

(a) σ-NOCV of W$_5$-NHC$_{Me}$; (b) and (c) π-NOCVs of W$_5$-NHC$_{Me}$; (d) σ-NOCV of W$_5$-NHPb$_{Me}$; (e) and
(f) π-NOCVs of W$_5$-NHPb$_{Me}$. Energy values in kcal/mol

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