

# ENERGY DECOMPOSITION ANALYSIS AND NATURAL ORBITAL FOR CHEMICAL VALENCE OF COMPLEXES WITH N-HETEROCYCLIC CARBENE AND ANALOGUES

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Received: 12 August 2013 ; Accepted for publication: 4 May 2014

## ABSTRACT

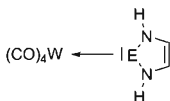
The natural of W-E bonding in group 14 compounds [(CO)<sub>4</sub>W-{NHE}] (W4-NHE) has been investigated by means of the Energy Decomposition Analysis-Natural Orbital for Chemical Valence (EDA-NOCV) method which combines charge (NOCV) and energy (EDA) partitioning schemes at the BP86/TZ2P+ level of theory. The EDA-NOCV results indicate that the decrease in bond strength from W4-NHC to W4-NHPb correlates with the decrease of  $\Delta E_{elstat}$  and  $\Delta E_{orb}$  and the trend of the W-E bond strength was W4-NHC > W4-NHSi > W4-NHGe > W4-NHSn > W4-NHPb. The decrease in the donation (CO)<sub>4</sub>W ← NHE, which is manifested in the calculated values for  $\Delta E_{\sigma}$  and in the electrostatic attraction,  $\Delta E_{elstat}$ , provides a rationale for the weaker bonding of the heavier atoms E. The bonding in the complexes with N-heterocyclic carbene and analogues W4-NHE exhibits the typical feature in terms of strong  $\sigma$ -donation and weak  $\pi$ -donation. All investigated complexes [(CO)<sub>4</sub>W-{NHE}] are suitable targets for synthesis which will open the door to a new field of experimental chemistry.

**Keywords:** donor-acceptor interaction; bonding analysis; energy decomposition analysis (EDA).

## 1. INTRODUCTION

Interest in carbon(0) compounds with N-heterocyclic carbene ligands has recently been revitalized by experimental and theoretical studies which open new light on the chemistry of this class of compounds. On the experimental site, the neutral donor-acceptor systems could be isolated and the structures were fully characterized by X-ray structure analysis [1]. Other divalent carbon(0) compounds with the general formula C(L)<sub>2</sub> that have L → C donor-acceptor bonds have been searched in the recent past [2]. A straightforward choice for L was N-heterocyclic carbene (NHCs), which are often compared with phosphanes as ligands in transition-metal chemistry [3]. The structures and bonding situation in transition metal complexes that carry N-heterocyclic carbene and analogues NHE where E = C – Pb have been recently investigated with the help of energy decomposition analysis (EDA) by some authors [4-7]. The fact is that geometrical structures and natural of chemical bonding of complexes that

carry ligands might exhibit significantly trend when versatile ligands connect with appropriate elements [5, 6] and change much in properties when extension from the slighter (C) to the heavier homologues (Si, Ge, Sn, Pb). Transition metal complexes turn out to be fascinating factors due to their flexibility in forming new bonds. Therefore, it is thus interesting to study the structures and the bonding situation of transition metal complexes that carry NHE ligands. This motivated us to investigate the bonding situation of main-group with transition metal chemistry. We have chosen examples of the group-14 compounds and  $W(CO)_4$  which exhibit the chemical bonding in complexes using EDA-NOCV method (Scheme 1). Herein we report on the first theoretical investigation of N-heterocyclic carbene and analogues with the general formula NHE. The calculations predict that the experimental unknown NHE compounds should be synthetically accessible species with promising chemical properties. We hope that the data give a well-defined quantitative answer to the questions about the strength of the divalent and electrostatic interactions and about the contribution of  $\sigma$  and  $\pi$  electrons to the donor-acceptor bond.



Scheme 1. Compounds investigated in this study:  $[(CO)_4W-\{NHE\}]$  (W4-NHE) with  $E = C - Pb$ .

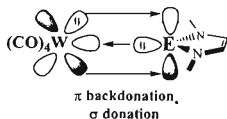
## 2. COMPUTATIONAL METHODS

The bonding analyses of the complexes were optimized with the program package ADF 2009.01 [8] at the BP86 level conjunction with a triple- $\zeta$ -quality basis set using uncontracted Slater-type orbitals (STOs) augmented by two sets of polarization function with a frozen-core approximation for the core electrons [9]. An auxiliary set of s, p, d, f, and g STOs were used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle [10]. Scalar relativistic effects were incorporated by applying the zeroth-order regular approximation (ZORA) [11]. This level of theory is denoted as BP86/TZ2P+. The nature of the W-E bonds in  $[(CO)_4W-\{NHE\}]$  was investigated at BP86/TZ2P+ with  $C_1$  symmetric geometries and fragmentation schemes which link the concepts of bond-order, bond-orbitals, and charge rearrangement of the EDA-NOCV method which combines the energy decomposition analysis (EDA) [12] with the Natural Orbitals for Chemical Valence (NOCV) [13].

## 3. RESULTS AND DISCUSSION

The nature of the W-E bonds was continuously analyzed using EDA-NOCV calculations to give insight into the chemical bonding between N-heterocyclic carbene - analogues NHE and  $W(CO)_4$ . This leads to a donor-acceptor description of the W-E bond. Therefore, the W4-NHE molecules are divided into the fragments NHE and  $W(CO)_4$ , and both are in the singlet state. Table 1 shows the numerical results of EDA-NOCV calculations for the W4-NHE complexes. The valence orbital interactions of the donor-acceptor bond between donor fragment NHE and acceptor fragment  $W(CO)_4$  in W4-NHE are shown in Scheme 2. Like the  $[(CO)_5W-\{NHE\}]$  (W5-NHE) system described in the recent past [2], the preparation energies  $\Delta E_{\text{prep}}$  vary very little between 1.5 kcal/mol (W4-NHSn) and 2.9 kcal/mol (W4-NHSi). The order is  $W4-NHC >$

W4-NHSi > W4-NHGe > W4-NHSn > W4-NHPb. The results of EDA-NOCV calculations for the tungsten-NHE bonds of W4-NHC – W4-NHPb are shown in Table 1. The decrease of the BDEs from the lighter to heavier adduct is determined by the intrinsic strength of the metal-ligand bonds  $\Delta E_{\text{int}}$ .



*Scheme 2.* Valence orbital interactions of the donor-acceptor bond between E and W in W4-NHE:  $\sigma$ -donation via the  $\sigma$ -lone-pair and weak  $\pi$ -donation from donor fragment NHE to acceptor fragment W(CO)<sub>4</sub>.

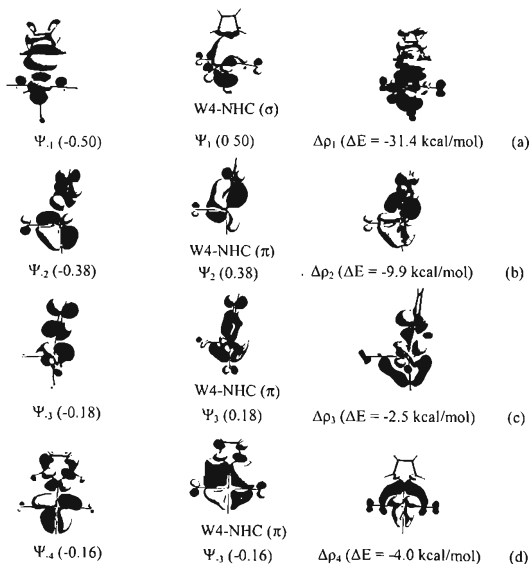
*Table 1.* EDA-NOCV results at the BP86/TZ2P+ level for compounds W4-NHC – W4-NHPb using the moieties [W(CO)<sub>4</sub>] and [NHE]. The complexes were analyzed with C<sub>1</sub> symmetry. Energy values in kcal/mol.

Compound	W4-NHC	W4-NHSi	W4-NHGe	W4-NHSn	W4-NHPb
Fragmentation	W(CO) <sub>4</sub> NHC	W(CO) <sub>4</sub> NHSi	W(CO) <sub>4</sub> NHGe	W(CO) <sub>4</sub> NHSn	W(CO) <sub>4</sub> NHPb
$\Delta E_{\text{int}}$	-63.0	-48.2	-37.5	-31.9	-27.3
$\Delta E_{\text{Pauli}}$	125.3	116.6	85.3	66.2	50.0
$\Delta E_{\text{elstat}}^{[a]}$	-133.3 (71.8%)	-104.1 (63.2 %)	-72.2 (58.8%)	-54.0 (55.0%)	-40.3 (52.2%)
$\Delta E_{\text{orb}}^{[a]}$	-52.4 (28.2%)	-60.7 (36.8%)	-50.6 (41.2%)	-44.1 (45.0%)	-36.9 (47.8%)
$\Delta E_{\sigma}^{[b]}$	-32.6 (62.2%)	-37.9 (62.4%)	-31.3 (61.9%)	-27.9 (63.3%)	-30.2 (81.8%)
$\Delta E_{\pi}^{[b]}$	-16.4 (31.3%)	-20.2 (33.3%)	-18.3 (36.2%)	-15.3 (34.7%)	-5.4 (14.6%)
$\Delta E_{\text{res}}^{[b]}$	-3.4 (6.5%)	-2.6 (4.3%)	-1.0 (1.9%)	-0.9 (2.0%)	-1.3 (3.6%)
$\Delta E_{\text{precp}}$	2.8	2.9	2.0	1.5	2.4
$\Delta E (= -D_c)$	-57.5	-45.3	-35.5	-30.4	-24.9

<sup>[a]</sup> The values in parentheses are the percentage contributions to the total attractive interactions  $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$

<sup>[b]</sup> The values in parentheses are the percentage contributions to the total orbital interactions  $\Delta E_{\text{orb}}$

Table 1 also shows that the Pauli repulsion  $\Delta E_{Pauli}$  has the largest value of 125.3 kcal/mol for W4-NHC and gets smaller from E = C to E = Pb (50.0 kcal/mol), which means that the decrease in bond strength comes from weaker attractive interactions. Moreover, the electrostatic term  $\Delta E_{elstat}$  continuously decreases from W4-NHC (-133.3 kcal/mol) to the heavier tetrylenes W4-NHSi (-104.1 kcal/mol), W4-NHGe (-72.2 kcal/mol) and it becomes weakest in the lead complex W4-NHPb (-40.3 kcal/mol). The same trend is shown for the orbital interactions, which indicates decreases in the orbital interactions, the percentage contribution of the orbital interactions increases from W4-NHC to W4-NHPb and the absolute values decrease as stated above. Two thirds of the value of  $\Delta E_{orb}$  comes from  $\sigma$ -contributions. The decrease in bond strength from W4-NHC to W4-NHPb correlates with the decrease of  $\Delta E_{elstat}$  and  $\Delta E_{orb}$ .



The plots of the pairs of orbitals  $\psi_k/\psi_k$  that yield the NOCVs providing the largest contributions to the  $\sigma$ - and  $\pi$ -orbital terms  $\Delta E_\sigma$  and  $\Delta E_\pi$  in W4-NHE ( $E = C, Pb$ ) and the associated deformation densities  $\Delta\rho$  and stabilization energies are shown in Figure 1 and Figure 2. The homologues W4-NHSi – W4-NHSn exhibit similar shapes to those of the lighter homologues (W4-NHC) and therefore, they are not shown in those figures. The shape of the NOCV pairs  $\psi_1/\psi_1$  and the deformation densities  $\Delta\rho_1$  of W4-NHC exhibit typical features for  $(CO)_4W \leftarrow NHE$   $\sigma$ -donation. Figure 1(a) shows that the  $\sigma$ -type interaction is clearly from the donating NHC fragment to the accepting  $W(CO)_4$  fragment. The deformation density reveals that the charge flow is from the NHC ligand toward the  $W(CO)_4$  fragment. Interpretation of the results for the  $\pi$ -type interaction is also straightforward. The shapes of the NOCV pairs  $\psi_2/\psi_2$  and  $\psi_4/\psi_4$ , and particularly the deformation densities  $\Delta\rho_2$  and  $\Delta\rho_4$  in Figure 1(b) and Figure 1(d) clearly show that stabilizations of -9.9 and -4.0 kcal/mol can be assigned to  $(CO)_4W \leftarrow NHC$   $\pi$ -donation in W4-NHC. The second ( $\psi_2/\psi_2$ ;  $\Delta\rho_2$ ) and the fourth ( $\psi_4/\psi_4$ ;  $\Delta\rho_4$ ) contributions are combinations of charge redistribution in the NHC and the  $\pi$ -donation from the  $(CO)_4W$  to the NHC. In contrast to this, the shape of the charge flow  $\Delta\rho_3$  indicates that the small stabilization of -2.5 kcal/mol exhibits typical features for  $(CO)_4W \leftarrow NHC$   $\pi$ -donation and the relaxation of the  $W(CO)_4$  fragment as shown in Figure 1(c). Thus, the bonding in the tetraylene complexes W4-NHE exhibits the typical feature in terms of strong  $\sigma$ -donation and weak  $\pi$ -donation.

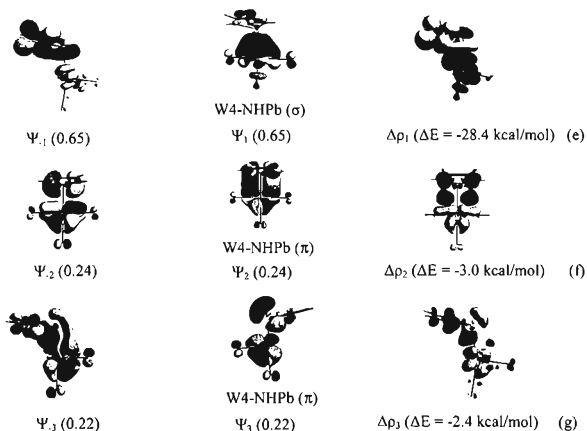


Figure 2. Most important NOCV pairs of orbitals  $\psi_k$ ,  $\psi_k$  with their eigenvalues  $-v_k$ ,  $v_k$ , which are given in parentheses, and the associated deformation densities,  $\rho_k$ , and orbital stabilization energies,  $\Delta E$ , for the complex W4-NHPb. The charge flow in the deformation densities is from the yellow  $\rightarrow$  blue region.

(e)  $\sigma$ -NOCV of W4-NHPb, (f) and (g)  $\pi$ -NOCVs of W4-NHPb.

Figure 2 shows significantly different EDA-NOCV results for W4-NHPb because of the surprising structure of the plumbylene ligand, which is bonded through its  $\pi$ -electron density. Figure 2(e) clearly shows that the  $\sigma$ -type interaction has the direction of the charge flow of  $(\text{CO})_4\text{W} \leftarrow \text{NHPb}$ . Like the plumbylene adduct  $[(\text{CO})_5\text{W} \cdot \{\text{NHPb}\}]$  (W5-NHPb) described by Nguyen [6], the shape of the  $\psi_1$  donor fragment of the NOCV pair of W4-NHPb suggests that  $\sigma$ -donation comes from the HOMO of NHPb which has  $\pi$ -symmetry with respect to the free ligand. In order to further explain about the bonding situation of the current system. We want to point out that the designation of  $\sigma$ - and  $\pi$ -orbitals of the ligands depends if they are considered as free molecules or as ligands in the transition metal complex.

This is because the designation of  $\sigma$ - and  $\pi$ -symmetry depends on the choice of the mirror plane which is used as reference for the assignment. An orbital may have  $\sigma$ -symmetry in a complex while it has  $\pi$  symmetry in the ligand, because the classification is made with regard to different mirror planes. For example, in the free NHE ligand it is the molecular plane which is used as reference for the assignment. In the complexes  $[(\text{CO})_5\text{W} \cdot \{\text{NHE}\}]$  (W5-NHE) [6], the reference plane contains the W-E axis and it bisects the plane of the P-E-P or NHE ligand. In this case, the significantly different binding mode of the NHPb ligand exhibits strange NOCV pairs compared with the lighter homologues.

The acceptor fragment  $\psi_1$  of W4-NHPb looks very similar to the  $\sigma$  acceptor fragments of W4-NHC (Figure 1). The deformation density  $\psi_1$  exhibits a small area of charge donation (yellow area) at the  $\text{W}(\text{CO})_4$  moiety associated with the deformation density  $\Delta\rho_1$  and a stabilization energy of -28.4 kcal/mol. Figure 2(f) and 2-g show that the very weak  $\pi$ -type orbital interactions in W4-NHPb come from typical  $\pi$ -donation  $(\text{CO})_4\text{W} \leftarrow \text{NHPb}$  and the relaxation of the  $(\text{CO})_4\text{W}$  fragment. The shape of the charge flow  $\psi_2/\psi_2$  and  $\psi_3/\psi_3$  indicates stabilization of -3.0 and -2.4 kcal/mol. From the above results, we can assert that the weaker bonds of the heavier complexes  $[(\text{CO})_4\text{W} \cdot \{\text{NHE}\}]$  result from a strong decrease in the electrostatic component of the W-E bonds. The  $\pi$ -interactions in  $[(\text{CO})_4\text{W} \cdot \{\text{NHE}\}]$  are due to very weak  $\pi$ -backdonation and are also irrelevant for the bond strength. The decrease in the donation  $(\text{CO})_4\text{W} \leftarrow \text{NHE}$ , which is manifested in the calculated values for  $\Delta E_\sigma$  and in the electrostatic attraction,  $\Delta E_{\text{elstat}}$ , provides a rationale for the weaker bonding of the heavier atoms E.

### 3. CONCLUSION

In summary, quantum-chemical calculations suggest that transition-metal complexes tetrylenes  $[(\text{CO})_4\text{W} \cdot \{\text{NHE}\}]$  ( $\text{E} = \text{C} - \text{Pb}$ ) should be synthetically accessible compounds with tetrylenes act as two-electron-donor ligands in transition-metal complexes. The EDA-NOCV calculations suggest that the trend of the W-E bond strength was  $\text{W4-NHC} > \text{W4-NHsi} > \text{W4-NHGe} > \text{W4-NHsn} > \text{W4-NHPb}$ . The EDA-NOCV indicates that the decrease in bond strength from W4-NHC to W4-NHPb correlates with the decrease of  $\Delta E_{\text{elstat}}$  and  $\Delta E_{\text{orb}}$ . The decrease in the donation  $(\text{CO})_4\text{W} \leftarrow \text{NHE}$ , which is manifested in the calculated values for  $\Delta E_\sigma$  and in the electrostatic attraction,  $\Delta E_{\text{elstat}}$ , provides a rationale for the weaker bonding of the heavier atoms E. The bonding in the complexes with N-heterocyclic carbene and analogues W4-NHE exhibits the typical feature in terms of strong  $\sigma$ -donation and weak  $\pi$ -donation. 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  $\sigma$ -donors and weak  $\pi$ -donors.

**Acknowledgements.** The jobs of this study were run via Erwin account which is excellent serviced by the Hochschulrechenzentrum of the Philipps-Universität Marburg-Germany. N.T.A.N thanks Prof. Dr. Gernot Frenking for allowing her to continuously use her own account at Frenking's group. Further computer time was provided by the HLRS Stuttgart, the HHLRZ Darmstadt, and the CSC Frankfurt.

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## TÓM TẮT

### PHÂN TÍCH NĂNG LƯỢNG PHÂN HỦY KẾT HỢP VỚI ĐIỆN TÍCH TRONG ORBITAL LIÊN KẾT HÓA TRỊ CỦA CÁC HỢP CHẤT CHỨA PHỐI TỬ N-HETEROCYCLIC CARBENE VÀ CÁC ĐỒNG ĐẲNG

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Bản chất liên kết hóa học của hệ phức chứa phối tử *N*-heterocyclic carbene và các đồng đẳng sau cacbon trong nhóm 14 [(CO)<sub>4</sub>W-{NHE}] (W4-NHE) với E = C, Si, Ge, Sn, Pb được tính toán bằng phương pháp phân tích năng lượng phân hủy kết hợp với điện tích trong orbital liên kết hóa trị (EDA-NOCV), với sự kết hợp giữa phần điện tích (NOCV) và phần năng lượng (EDA) ở mức BP86/TZ2P+. Kết quả EDA-NOCV chỉ ra rằng độ mạnh của liên kết W-E trong các hợp chất nghiên cứu giảm dần từ W4-NHC đến W4-NHPb tương ứng với sự giảm các mức năng lượng tương tác tĩnh điện  $\Delta E_{\text{elstat}}$  và năng lượng tổng của các orbital tham gia liên kết  $\Delta E_{\text{orb}}$ . Năng lượng phân ly liên kết của liên kết chính W-E cho thấy, liên kết W-C mạnh nhất và giảm dần từ C đến Pb: W4-NHC > W4-NHSi > W4-NHGe > W4-NHSn > W4-NHPb. Các phân tích về cấu trúc và tính chất của hệ phức nghiên cứu chỉ ra rằng các liên kết W-E được hiển thị đặc trưng bằng sự cho electron (CO)<sub>4</sub>W ← NHE, được thể hiện qua các giá trị của năng lượng tổng của các orbital tham gia liên kết  $\Delta E_{\text{orb}}$  và mức năng lượng tương tác tĩnh điện  $\Delta E_{\text{elstat}}$ , là cơ sở cho việc mô tả đầy đủ bản chất của các liên kết yếu của các đồng đẳng sau cacbon trong nhóm 14 với E = Si, Ge, Sn, Pb. Tính chất đặc trưng của phối tử NHE là “mạnh-liên kết σ cho và yếu-liên kết π cho” (strong σ-donation and weak π-donation). Cấu trúc và tính chất của các hệ phức chứa phối tử *N*-heterocyclic carbene và các đồng đẳng sau cacbon trong nhóm 14 [(CO)<sub>4</sub>W-{NHE}] trong nghiên cứu lý thuyết này hoàn toàn phù hợp để định hướng cho các phản ứng tổng hợp với việc mở ra một hướng nghiên cứu mới cho các nghiên cứu thực nghiệm.

**Từ khóa:** tương tác cho nhận; phân tích liên kết; năng lượng phân hủy (EDA).